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Encyclopedia of...

REFERENCE BOOK
NOT TO BE LENT

Kirk-Othmer

ENCYCLOPEDIA
OF CHEMICAL
TECHNOLOGY

Second Edition

VOLUME 1

A to Aluminum

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Encyclopedia of..

CONTENTS

ABHERENTS, 1	ACTINIDES, 351
ABLATION, 11	ADHESIVES, 371
ABRASIVES, 22	ADIPIC ACID, 405
ABSORPTION, 44	ADSORPTION, 421
ACETALDEHYDE, 77	AEROSOLS, 470
ACETAL RESINS, 95	AIR CONDITIONING, 481
ACETALS AND KETALS, 107	ALCOHOLIC BEVERAGES, DISTILLED, 501
ACETATE AND TRIACETATE FIBERS, 109	ALCOHOLS, 531
ACETIC ACID DERIVATIVES, 138	ALCOHOLS, HIGHER, FATTY, 541
ACETOACETIC ACID AND ESTER, 153	ALCOHOLS, HIGHER, SYNTHETIC, 560
ACETONE, 159	ALCOHOLS, POLYHYDRIC, 569
ACETOPHENONE, 167	ALCOHOLS, UNSATURATED, 598
ACETYLENE, 171	ALDEHYDES, 639
ACID ANHYDRIDES, 211	ALGAL CULTURES, 649
ACID-BASE SYSTEMS, 213	ALKALI AND CHLORINE INDUSTRIES, 668
ACID HALIDES, 222	ALKALOIDS, 758
ACIDS, CARBOXYLIC, 224	ALKANOLAMINES, 809
ACIDS, DICARBOXYLIC, 240	ALKOXIDES, METAL, 832
ACROLEIN AND DERIVATIVES, 255	ALKYD RESINS, 851
ACRYLAMIDE, 274	ALKYLATION, 882
ACRYLIC ACID AND DERIVATIVES, 285	ALKYLPHENOLS, 901
ACRYLIC AND MODACRYLIC FIBERS, 313	ALLYL COMPOUNDS, 916
ACRYLONITRILE, 338	ALUMINUM AND ALUMINUM ALLOYS, 929

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PREFACE TO THE SECOND EDITION

The first edition of the Encyclopedia of Chemical Technology appeared in fifteen volumes, of which Volume 1, A to Anthrimides, was published in 1947, and the final volume, including the Index, in 1956. The years 1957 and 1960 saw the appearance of the First and Second Supplement Volumes, in which certain subjects were treated again, giving more up to date information.

It goes without saying that the entire first edition of the Encyclopedia is now in need of further treatment. This is especially true of the earlier volumes, containing the earliest letters in the alphabet. Volume 1 of the second edition, A to Aluminum, appears when Volume 1 of the first edition is already sixteen years old; by maintaining a similar schedule for the succeeding volumes of the second edition, each will be separated by a comparable time interval from the corresponding volume in the first edition.

The second edition of the Encyclopedia of Chemical Technology is more than just a revision of the first; it could be called a completely new encyclopedia. All the technological articles have been rewritten, in some cases by the same author who wrote in the first edition, in some cases by a different author. In all cases, the author has conceived of the article so as to present up-to-date chemical technology. In doing this, it often happened that certain passages from the first edition could be used unchanged, or with very little change. This was often possible, for example, in sections on History; sometimes, in sections on Physical and Chemical Properties; or in other sections. For all articles in the second edition which have a counterpart article in the first edition, the name and affiliation of the first-edition author are noted. Grateful acknowledgment is made here to the first-edition authors, for those cases where portions of their texts have been used with little or no change.

Although the general scheme of the Encyclopedia has not been changed, the list of titles is not exactly the same: The first two articles in this volume, Abherents and Ablation, are entirely new, and other changes have been made whenever, for any reason, this appeared suitable. For example, Volume 1 of the first edition contained Alcohol, industrial, but in the second edition this subject will be found under Ethanol.

Changes in format, between the first and second editions, are relatively minor. However, the reader will find, in one respect, a certain change in emphasis: The first edition concentrated on presenting United States technology; but in the second edition a number of the articles have been contributed from abroad, and the intention has been to present chemical technology, wherever it is found, without regard to national boundaries.

INTRODUCTION

The main subject of the Encyclopedia is chemical technology, and about one half of all the articles deal with chemical substances, either single substances, such as Sulfuric acid, or groups of substances, such as Aluminum compounds. There are also articles on industrial processes, such as Carbonization of coal; on uses, such as Adherents, Adhesives; on pharmaceuticals, dyes, fibers; on foods and other human uses, such as Cosmetics. There are articles on the unit operations and unit processes of chemical engineering; on fundamentals, such as Thermodynamics, Heat transfer, Film theory; on methods of analysis; and on scientific subjects, such as Catalysis, Color and constitution, Magnetic properties, and Stereochemistry. Still other articles deal with such general subjects as Computers, Literature of chemistry, Patents, or Transportation.

In general, the properties and manufacture of any substance are given in one article, which makes cross reference to one or more articles where the uses of that substance are described. Thus, the manufacture of fused alumina is described under Aluminum compounds, but for its uses the reader will be directed to such articles as Abrasives, Refractories.

For inorganic compounds, in some cases it is the anion, in others the cation that has the greater industrial significance. Thus, calcium phosphate, sodium phosphate, and ammonium phosphate are important primarily as phosphates and are discussed under Phosphoric acid and phosphates. Similarly, chromates and borates are under Chromium compounds and Boron compounds, respectively, and salts of organic acids (except acetates and formates) are discussed with the acids. On the other hand, barium chloride, barium nitrate, and barium sulfate would be thought of together and are therefore described in Barium compounds. In general, compounds of the following anions are dealt with in articles such as Aluminum compounds and Calcium compounds: acetates; carbonates; formates; chlorides, bromides and iodides (under halides); nitrates; nitrites; oxides (including hydroxides and oxygen acids and their salts, but excluding true peroxides); sulfates; sulfites; and sulfides. The organic compounds of a metal, containing a metal-to-carbon bond, are also discussed with the compounds of that metal. However, fluorine, in its industrial applications, is so different from the other halogens that the metallic fluorides are usually grouped together under Fluorine compounds, inorganic.

Organic compounds containing fluorine (with or without other halogens) are discussed under Fluorine compounds, organic, and there are articles on Bromine

compounds, organic, and Iodine compounds, organic. Chlorine is treated somewhat differently: The article Chlorocarbons and chlorohydrocarbons covers a large number of industrially important compounds; compounds containing other elements as well as carbon, hydrogen, and chlorine are sometimes grouped together (as, Chlorophenols; Chlorohydrins), sometimes treated as derivatives under a parent compound (thus chloroacetophenone appears as a derivative under Acetophenone).

In general, the treatment of a compound will be found either under its own name, or under a group of substances (for example, ethyl acetate under Esters, organic), or as a derivative under a parent compound (for example, *p*-aminobenzoic acid under Benzoic acid). The cross references provided will, it is hoped, in almost all cases direct the reader to the appropriate part of the Encyclopedia.

ABBREVIATIONS AND SYMBOLS

A	angstrom unit(s) (after Ångström)	ar-	aromatic (eg, <i>ar</i> -derivatives of tetrahydronaphthalene)
A	anion (eg, HA)	Ar	aryl
AATCC	American Association of Textile Chemists and Colorists	as-	asymmetric(al)
abs	absolute	ASA	American Standards Association
ac	alternating current	ASHRAE	American Society of Heating, Refrigeration and Air-Conditioning Engineers
ac-	alicyclic (eg, <i>ac</i> -derivatives of tetrahydronaphthalene)	ASM	American Society for Metals
accel(d)	accelerate(d)	ASME	American Society of Mechanical Engineers
acceln	acceleration	ASTM	American Society for Testing and Materials
ACS	American Chemical Society	atm	atmosphere(s), atmospheric
addn	addition	at. no.	atomic number
AGA	American Gas Association	at. wt	atomic weight
ah,		av	average
amp-hr	ampere-hour(s)	b	barn(s)
AIChE	American Institute of Chemical Engineers	b(as in b ₁₁)	boiling (at 11 mm)
AIME	American Institute of Mining and Metallurgical Engineers	bbl	barrel(s)
AIP	American Institute of Physics	BC	body-centered
alc	alcohol(ic)	Bé	Baumé
alk	alkaline (not alkali)	Bhn	Brinell hardness number
Alk	alkyl	bp	boiling point
amp	ampere(s)	Btu	British thermal unit(s)
amp-hr,		bu	bushel(s)
ah	ampere-hour(s)	C	centigrade; curie
amt	amount (noun)	C-	denoting attachment to carbon (eg, <i>C</i> -alkyl derivatives of aniline)
anhyd	anhydrous	ca	circa, approximately
API	American Petroleum Institute	cal	calorie(s)
app	apparatus	calcd	calculated
approx	approximate(ly)		
aq	aqueous		

cfm,		dc	direct current
ft ³ /min	cubic foot (feet) per minute	dec,	
cg	centigram(s)	decomp	decompose(s)
cgs	centimeter-gram-second	decompd	decomposed
chem	chemical	decompn	decomposition
CI	Colour Index (number); the CI numbers given in <i>ECT</i> , 2nd ed., are from the new <i>Colour Index</i> (1956) and Suppl. (1963), <i>Soc. Dyers Colourists</i> , Bradford, England	den	denier
		den/fil	denier per filament
		deriv	derivative
		detd	determined
		detn	determination
		diam	diameter
		dielec	dielectric (adj.)
cks	centistokes	dil	dilute
cl	car lots	distd	distilled
cm	centimeter(s)	distn	distillation
coeff	coefficient	dl	deciliter
compd,		dl-, DL-	racemic
cpd	compound (noun)	dm	decimeter
compn	composition	dp	dewpoint
concd	concentrated	e	electron
concn	concentration	ed.	edited, edition, editor
cond	conductivity	elec	electric(al)
const	constant	emf	electromotive force
cont	continued	en	entropy unit(s)
cor	corrected	eng	engineering
cp	chemically pure	equil	equilibrium(s)
cp(s)	centipoise(s)	equiv	equivalent
cpd,		esp	especially
compd	compound (noun)	est(d)	estimate(d)
crit	critical	estn	estimation
cryst	crystalline	esu	electrostatic unit(s)
crystd	crystallized	ev	electron volt(s)
crystn	crystallization	expt(l)	experiment(al)
cu	cubic	ext(d)	extract(ed)
d	density (conveniently, specific gravity)	extn	extraction
d	differential operator	F	Fahrenheit
d-	dextro-, dextrorotatory	FC	face-centered
D-	denoting configurational relationship (as to dextro-glyceraldehyde)	Fed, Fedl	Federal (as in Fed Spec)
db	decibel; dry-bulb	fl oz	fluid ounce(s)
		fob	free on board
		fp	freezing point

frz	freezing	kv	kilovolt(s)
ft	foot (feet)	kv-amp	kilovolt-ampere(s)
ft-c	foot-candle	kw	kilowatt(s)
ft ³ /min, cfm	cubic foot (feet) per minute	kw-hr	kilowatt-hour(s)
ft-lb	foot-pound(s)	l	liter(s)
g	gram(s)	l-	<i>levo</i> -, levorotatory
g	gravitational acceleration	L-	denoting configurational relationship (as to <i>levo</i> - glyceraldehyde)
gal	gallon(s)	lb	pound(s)
g/den	gram(s) per denier	LC ₅₀	concentration lethal to 50% of the animals tested
gem-	geminal (attached to the same atom)	lcl	less than car lots
g-mol	gram-molecular (as in g-mol wt)	LD ₅₀	dose lethal to 50% of the animals tested
g-mole	gram-mole	liq	liquid
hp	horsepower	ln	logarithm (natural)
hr	hr(s)	log	logarithm (common)
hyd	hydrated, hydrous	m	meter(s)
hyg	hygroscopic	m-	meta (eg, <i>m</i> -xylene)
i, insol	insoluble	M	metal
i ⁱ (eg, Pr ⁱ)	iso (eg, isopropyl)	M	molar (as applied to concentration; not molal, which is written out)
i-	inactive (eg, <i>i</i> -methionine)	ma	milliampere(s)
IACS	International Annealed Copper Standard	manuf	manufacture
ibp	initial boiling point	manufd,	
ICC	Interstate Commerce Commission	mfd	manufactured
ICT	International Critical Tables	manufg,	
ID	inner diameter	mfg	manufacturing
in.	inch(es)	max	maximum
insol, i	insoluble	MCA	Manufacturing Chemists' Association
IPT	Institute of Petroleum Technologists	mcf	million cubic feet
IU	International Unit(s)	mech	mechanical
IUPAC	International Union of Pure and Applied Chemistry	meq	milliequivalent(s)
K	Kelvin	Mev	million electron volts
K	dissociation constant	mfd,	
kcal	kilogram-calorie(s)	manufd	manufactured
kev	kilo electron volt(s)	mfg,	
kg	kilogram(s)	manufg	manufacturing
		mg	milligram(s)
		min	minimum; minute(s)

misc	miscellaneous	oz	ounce(s)
mixt	mixture	<i>p</i> -	para (eg, <i>p</i> -xylene)
ml	milliliter(s)	pdr	powder
MLD	minimum lethal dose	pos	positive (adj.)
mm	millimeter(s)	powd	powdered
mM	millimole(s)	ppm	parts per million
mo(s)	month(s)	ppt(d)	precipitate(d)
mol	molecule, molecular	pptn	precipitation
mol wt	molecular weight	Pr. (no.)	Foreign prototype (number); dyestuff designation used in <i>AATCC Year Books</i> for dyes not listed in the old <i>Colour Index</i> (1924 ed.; 1928 Suppl.); obsolete since new <i>Colour Index</i> was published (1956 ed.; 1963 Suppl.)
mp	melting point	prepd	prepared
mph	miles per hour	prepn	preparation
MR	molar refraction	psi	pound(s) per square inch
mv	millivolt(s)	psia	pound(s) per square inch absolute
m μ	millimicron(s)	psig	pound(s) per square inch gage
ⁿ (as Bu ⁿ),		pt	point
<i>n</i> -	normal (as, normal butyl)	pts	parts
<i>n</i> (as, <i>n</i> _D ²⁰)	index of refraction (for 20°C and sodium light)	qual	qualitative
<i>n</i> -, ⁿ	normal (eg, <i>n</i> -butyl)	quant	quantitative
<i>N</i>	normal (as applied to concentration)	qv	which see (quod vide)
<i>N</i> -	denoting attachment to nitrogen (eg, <i>N</i> -methylaniline)	<i>r</i>	roentgen
neg	negative (adj.)	<i>R</i>	univalent hydrocarbon radical (or hydrogen); Rankine
NI	<i>National Formulary</i> (American Pharmaceutical Association, Washington, D.C.)	rep	roentgen(s) equivalent physical
NMR	nuclear magnetic resonance	resp	respectively
NND	<i>New and Nonofficial Drugs</i> (American Medical Association)	rh	relative humidity
no.	number	RI	Ring Index (number); from <i>The Ring Index</i> , Reinhold Publishing Corp., N.Y., 1940
NOIBN	not otherwise indexed by name (ICC specification for shipping containers)	rpm	revolutions per minute
<i>o</i> -	ortho (eg, <i>o</i> -xylene)	rps	revolutions per second
(<i>O</i>)-	denoting attachment to oxygen (eg, <i>O</i> -acetylhydroxylamine)		
(OD)	outer diameter		
owf	on weight of fiber		

RR1	New Ring Index (number); from <i>The Ring Index</i> , Reinhold Publishing Corp., N.Y., 1960		pressure (760 mm Hg, 0°C)
RT	room temperature	subl	sublime(s), subliming
s, sol	soluble	SUs	Saybolt Universal second(s)
^s (eg, Bu ^s), secondary (eg, secondary sec- butyl)		<i>sym</i> -, <i>s</i> -,	symmetrical (eg, <i>sym-m</i> - xylidene)
<i>s</i> -, <i>sym</i> -	symmetrical (eg, <i>s-m</i> - xylidene)	<i>t</i> , temp	temperature
<i>S</i> -	denoting attachment to sulfur (eg, <i>S</i> -methyl- cysteine)	^t (as, Bu ^t), <i>t</i> -, <i>tert</i> -	tertiary (eg, tertiary butyl)
SAE	Society of Automotive Engineers	<i>t</i> -, <i>tert</i> -, ^t	tertiary (eg, <i>t</i> -butyl)
satd	saturated	TAPPI	Technical Association of the Pulp and Paper Industry
satn	saturation	tech	technical
SCF	standard cubic foot (feet) (760 mm Hg, 60°F)	temp, <i>t</i>	temperature
Sch	Schultz number (designa- tion for dyes from <i>Farb- stofftabellen</i> , 4 vols., Akademie Verlag, Leipzig, 1931-1939)	<i>tert</i> -, <i>t</i> -, ^t	tertiary (eg, <i>tert</i> -butyl)
sec	second(s)	theoret	theoretical
<i>sec</i> -, ^s	secondary (eg, <i>sec</i> -butyl)	Twad	Twaddell
SFs	Saybolt Furol second(s)	USP	(<i>The</i>) <i>United States Pharmacopeia</i> (Mack Publishing Co., Easton, Pa.)
sl <i>s</i> , sl sol	slightly soluble	uv	ultraviolet
sol, <i>s</i>	soluble	v	volt(s)
soln	solution	var	variety
soly	solubility	<i>vic</i> -	vicinal (attached to adjacent atoms)
sp	specific	vol	volume(s) (not volatile)
sp, spp	species (sing. and pl.)	v <i>s</i> , v sol	very soluble
spec	specification	vs	versus
sp gr	specific gravity	w	watt(s)
sq	square	xu (ca 10 ⁻¹¹ cm)	x unit(s)
STP	standard temperature and	yd	yard(s)
		yr	year(s)

A

ABACA FIBER. See Fibers, vegetable.

ABHERENTS

Abherents or release agents (parting agents) are defined as solid or liquid films that reduce or prevent adhesion between two surfaces. Industrial fields in which abherents have attained great importance include metal casting and processing, food preparation and packaging, rubber and polymer processing, paper coating, the production of pressure-sensitive tapes, and glass fabrication. A number of factors influence adhesion of two materials to each other. The most important ones are penetration, chemical reaction and compatibility, low surface tension, surface configuration, and polarity differences between the two materials. Two solid surfaces generally do not adhere to each other because wetting does not take place and neither does penetration of one into the other. The only exception occurs when one of the surfaces is "tacky" or when chemical reaction takes place between the two surfaces at the interface. Frequently high static charges can also lead to adhesion. Therefore, the use of abherents becomes of technical importance when a solid and a liquid, or even more so, when a solid and a paste or dough form an interface and adhere to each other. For many centuries adhesion of a highly viscous material (paste, dough) has been a disturbing factor in the home in baking and cooking. Abherents in the form of fats, oils, or solids like flour have been used in order to prevent the sticking of dough to wooden kneading boards or to various metal baking dishes. With the greater industrial use of polymeric materials, both natural and synthetic, and also with the industrialization of baking, the commercial use of abherents has become widespread. As a matter of fact, some industries which are of great importance today could not have developed without the availability of modern abherents. As an example let us mention the pressure-sensitive tapes, which could not be unwound if the tape backing were not coated with a release agent.

Properties Required of an Abherent. Since many of the factors causing adhesion are of a chemical nature, one of the first requirements of a good abherent is complete chemical inertness toward the two materials whose adhesion is to be prevented. Adhesion is often due to opposing polarities of the surfaces, therefore the polarity relation of the abherent and of one or both of the surfaces in contact with it have to be taken into consideration in the choice of an abherent. Besides these two factors one physical property is of great importance, namely, good spreading ability (low surface tension), so that the abherent will form a continuous film between the surfaces and in this

way exclude any contact between the two materials. An extremely important factor in this action of abherents is temperature dependence. This dependence is so pronounced that a material which is an abherent at, for example, room temperature may act as an adhesive at elevated temperatures. A good example of this type of action is given by polyethylene film, which is used as an abherent layer to prevent the adhesion of uncured rubber slabs or preforms to each other. This same polyethylene film, above its softening point at approximately 100°C , will act as an excellent hot-melt adhesive. Another factor to be considered is volatility. Water would fulfill many of the requirements of an abherent, but because of its vaporization and the increased water absorption of many materials at elevated temperatures, water in most cases is not suited as an abherent. With knowledge of all these factors, we can now narrow down considerably the choice of an abherent. It has to (1) be chemically inert toward the two adhering materials, (2) have good spreading properties for one or both of the surfaces, (3) have low volatility at the temperature at which it is to be used.

In many cases adhesion is caused primarily by the physical configuration of the solid surface, namely, by its high porosity or roughness, which will tend to anchor a viscous material into the surface. In this case a powdered solid material will serve well as an abherent by filling the pores or smoothing out the roughness of a surface. Another example of the usefulness of solid abherents is adhesion caused by the moisture content or surface wetness of a dough; in this case, the solid abherent serves to dry the surface and in this way prevents adhesion.

It is obvious that a liquid, to be effective as an abherent between two materials, will have to spread so as to form a continuous film between the contacting surfaces. Therefore, an additional requirement for a good abherent is a low to medium viscosity at the temperature of application. There is an exception to this requirement, namely, where polymer melt flow is induced by high pressures. In this case an abherent of higher viscosity is more desirable so that it is not pushed aside and displaced by the polymer melt.

Methods for Applying Abherents. As mentioned previously, one of the most important systems in which abherents are used is at the interface of a solid and a dough or paste (polymer melt).

Three basic methods for the application of an abherent in this system are (a) spraying, brushing, or dusting a powdered solid or liquid abherent to the solid surface (b) producing a permanent abherent by baking an abherent polymeric surface to the solid surface or (c) incorporating the abherent in the polymer. In this latter case an abherent has to be chosen that is partly compatible with the polymer, at least at room temperature, and that will exude to some extent at the melt temperature in order to be available at the interface where adhesion has to be prevented. Many polymers will show a slight amount of tack even in the solid stage. This property has caused considerable difficulties in the processing of some polymeric materials. A good example is given by polyethylene films, which tend to adhere to each other because of static electricity and also because of cold flow. Polyvinyl chloride films show the same behavior. Therefore, the incorporation of abherents into these polymers before they are processed into films is standard practice. In the case of polyvinyl chloride they have become known as slip agents, whereas in the polyethylene field they have become known as slip agents, although in either case they really serve the same functions.

Industrial Fields Using Abherents

Metal Processing. Two metal-forming processes depend heavily on the use of abherents for their proper functioning. One is *die casting*, in which a rather low-melting alloy is molded under high pressure by transferring the melt to a steel mold and cooling under hydraulic pressure. Abherents are generally sprayed onto the mold surface in order to prevent the casting from sticking to the mold. Because of the high temperatures involved (above 800°F), silicones are the preferred abherents. The other metal-forming method which depends heavily on the use of abherents is the so-called *shell-molding* process. In this process a metal pattern or master is used, around which is poured a sand and resin combination which eventually forms the mold for casting the metal part. The metal pattern or master has to be re-used many times to form new shells, and fast and easy release of the shell from the pattern is therefore of great importance. Here again silicones have made an important place for themselves. A new pattern is usually coated with a curable silicone paste and, in continuous use, is usually recoated by spraying with a silicone emulsion after each cycle.

Silicone greases are also used to coat oven conveyors, dollies, carts, and other handling equipment that must operate under high-temperature conditions. The use of release agents in shell molding has led to tremendous improvements in this operation since the sticking of sand to the pattern after curing has been very detrimental and has slowed down the operation, necessitating cleaning of the patterns after each use.

Release agents are also used in the metal industry for the molding or casting of ingots from zinc, brass, bronze, lead, and precious metals. The release agents, primarily silicones, are applied to the mold in order to give easier release of the castings and to avoid build ups in the molds.

Food Industry. As mentioned above, release agents have been used for centuries in the baking and frying of various foods. In this case the choice of an abherent was, of course, limited to edible materials. In very recent years however, the use of inert coatings for baking or frying pans has been more and more accepted. Frying pans for the home are now available with a polytetrafluoroethylene coating, which is permanent if treated carefully and not injured by handling with metal tools. In industrial baking, where vegetable oils and fats have been used for many centuries, a tremendous improvement has been achieved by coating baking pans with a silicone varnish which gives the pan long-term abherent properties.

Rubber Processing. See Elastomers, synthetic; Rubber, natural. Abherents have attained extreme importance in the processing of rubber. Generally, both natural and synthetic rubbers have excellent adhesive qualities in the uncured stage, yet these rubbers have to be processed and shaped before they can be cured. There are a great variety of processing steps involved in the manufacture of rubber goods. Generally the procedure may be broken down as follows: First, natural, synthetic, or mixtures of both rubbers are blended with various compounding ingredients, such as fillers, accelerators, vulcanizing agents, pigments, and other ingredients that go into specific rubber compounds. This is usually accomplished in an internal mixer of the Banbury type. Then, this mixed batch of rubber is generally sheeted through a rubber mill to put it into the form of a sheet or slab, which may then be calendered or molded into thinner sheets, extruded into tubing, or formed into other preforms for molded

rubber goods. During these processing steps that precede vulcanization, the rubber compounds would tend to stick to metal surfaces and even more so to each other. In order to prevent this sticking, coated papers and coated cloths have been used for many years to separate the individual layers of uncured rubber. Also, ever since rubber processing has become an industrial art, various abherents have been used to dust or spray onto the molds. Abherents have also been incorporated into the compounds to reduce tackiness. All of the various types of abherents have been and are still being used in the rubber industry. Of primary importance are the various metal stearates, stearic acid, oleic acid, microcrystalline and paraffin waxes and other synthetic waxes, like the stearamides, alkyl *N*-substituted stearamides, and bis-stearamides (derived from diamines, eg, ethylenediamine), and ester waxes, such as montan wax. In rubber processing, as in many other fields where abherents have been employed, the advent of the silicones has brought about major changes. Previously, molds for molding rubber goods or for curing rubber sheeting had been dusted after each cycle with zinc stearate, calcium stearate, and similar abherents. These have mostly been replaced by silicones in the form of water dispersions, which are sprayed onto the molds in dilutions of 1% or below. Whereas previous lubricants had led to build up of crusts in the molds and had necessitated frequent cleaning, the silicones have eliminated this shortcoming completely. One other use of abherents in the rubber industry is the dusting of finished unfilled rubber goods which would be tacky without a surface application of abherent. In this case solid materials have been found to serve best; talcum, mica, finely dispersed silicates, or metallic stearates have proved advantageous.

Stearic acid, one to five parts per hundred of rubber, usually forms part of any rubber formulation. The function of this fatty acid is not completely clear. It is assumed that the stearic acid contained in both natural and synthetic rubbers, in addition to that which is added to the compound, reacts with the zinc oxide present in every formulation during vulcanization; furthermore, that the zinc stearate thus formed, in turn, reacts with the accelerator, enabling the latter to promote the vulcanization. Without any doubt the addition of fatty acid also produces an abherent effect in this case.

Polymer Processing. The use of abherents is of the utmost importance in polymer processing. Some polymers have particularly great adhesive properties at or about their melting points and are, therefore, in greater need of abherents than others. Examples of these highly adhesive melts are polystyrene, some polyolefins, other hydrocarbon resins, methyl methacrylate, and, to some extent, polyamides. But even polymers with lower adhesive forces require the use of release agents in most cases. The above-mentioned polymers, which are all thermoplastic in nature, are not anywhere near as high in their adhesive properties as some thermosetting resins that have to be cured in contact with the mold surface. Examples of these latter are the polyesters, polyurethanes, and polyepoxides.

The use of abherents in polymer processing extends to all possible ways of application. Most polymeric compounds made by the raw material manufacturers already contain abherents. Furthermore, the processor who adds pigments and other ingredients to the raw resins also adds abherents at that stage. In many cases the fabricator who molds or extrudes thermoplastics will tumble some release agent or abherent onto the molding powders or granules before melting them in the processing equipment. Even beyond this preparatory addition of abherents, an application of abherents to the mold surfaces or metal surfaces of other processing equipment is frequently necessary. From the number of ways in which abherents are added to poly-

mers, the importance of these products in various stages of polymer processing becomes apparent.

In order to illustrate the application of abherents, a few specific examples will be cited. In the injection molding of polystyrene, which is the greatest volume injection-molding material in use, abherents are added when the raw material is processed. Pure polystyrene as it comes out of the polymerization process needs the addition of abherents to promote the conversion of the raw polymer into molding pellets or granules. This conversion, which is usually accomplished through an extruder, is greatly facilitated by the addition of small amounts of abherents (metallic stearates, stearic acid). The increase in throughput through the extruder, when materials containing abherents are compared to those not containing any, can be as much as 20%. These molding pellets or granules, after they have been cooled, are again tumbled with a parting agent, which more or less adheres to the surfaces of the individual pellets. In this case a great variety of abherents can be applied. Zinc stearate, stearic acid, and stearamide are among the products most frequently used, but room-temperature liquids such as butyl stearate, are also employed in many cases.

In the injection-molding process unmelted molding pellets are pushed by a hydraulic ram into a cylinder where they are gradually heated and melted. It is the function of the abherent to reduce the friction of the granules against each other and also against the metal surfaces of the cylinder in order to reduce the pressure needed to convey them forward into the melting zone. This polymer melt is then injected by the ram into a cold form or mold. As soon as the polymer melt has sufficiently solidified, this shaped item can be removed from the form and the added abherent again helps tremendously in releasing the item from the metal surface. Nevertheless, in many cases additional abherents or release agents have to be applied to the mold surface in order to further facilitate the release of the molded polymeric article from the metal mold. It can easily be seen that the function of abherents in facilitating the molding of a polymer will also reduce the temperature to which the material has to be heated for it to flow properly into the mold. Since high temperatures are detrimental to the stability of most polymers, the abherents therefore also have a protective function, and result in articles of greater strength and quality. It should be noted that silicones are not used as abherent additives to polymers. The reason is that silicones are so powerful as abherents and so inert and noncompatible that their addition to polymers would counteract the cohesive forces and destroy the homogeneity of the material.

Silicones make very effective abherents when applied to the mold in the injection or compression molding of plastic materials but they have to be used with great caution, because molded polymeric items often have to be adhered to other surfaces, or lacquers have to be applied to them for decorative purposes. Silicones remaining on the surface of these molded pieces would seriously interfere with the above-mentioned aftertreatments.

In the processing of rigid and flexible polyvinyl chloride, abherents are also of great importance although polyvinyl chloride does not have as strongly adhesive a character in the melted state as polystyrene. In the manufacture of films from polyvinyl chloride, the compounds are generally blended in a cold or somewhat heated blender. They are then melted and fused on a heated rubber mill or in an internal mixer. This melt is then fed into a calender consisting of three or four heated rolls through which the polyvinyl chloride compound is squeezed down to the thickness desired in the finished film. For calendering, abherents have to be skillfully compounded into any poly-

vinyl chloride material, in order to make the melt follow the proper rolls and to make it release from the ones that should not be followed. Frequently the use of one abherent is not sufficient, and a combination of two or more have to be applied. An additional function of the abherent lies in the prevention of blocking or sticking of the film to the next layer in the roll of the finished film. Whereas small amounts of stearic acid provide excellent release from metal surfaces, other abherents, like calcium stearate, lead stearate, and stearyl amides are added to provide a combination of release from metal and antiblocking properties. These latter abherents will also greatly influence the surface appearance of the calendered film, providing such desirable properties as gloss and smoothness.

In the extrusion of polyvinyl chloride, a process that consists in melting a granulated or powdered polyvinyl chloride compound between a cooled rotating screw and a heated cylinder and in then pushing this homogenized heated melt through a shaping orifice, the addition of abherents will help release the compound from the rotating screw and in this fashion greatly increase the speed with which the compound is conveyed through the extruder cylinder. The abherents will also reduce the possibility of thermal breakdown, which is critical with polyvinyl chloride. Since the shaping orifice or die is usually the hottest part of the extruder, easier release from this hot and normally glossy surface is provided by coating the die surface with a silicone paste or grease prior to extrusion. This serves to fill in the pores of the metal and to prevent carbonization of the polymer melt as a result of prolonged contact with the hot metal. Coating of the die surface with abherent, however, is no substitute for the addition of various abherents to the compound itself.

In the casting of thermosetting plastic materials, such as polyesters and polyepoxides, it is most essential to provide easy release from either the male mold over which such a compound is cast or the female mold and flexible bag in which it is molded. Matched metal molds are also sometimes used to shape these compounds. Polyepoxides are known to be outstanding adhesives. Where release from a mold surface has to be provided, the use of abherents in one fashion or another is an absolute necessity. It is interesting to note that, in this field of casting thermosetting materials, the use of polymeric films as abherents, in the form of extruded or cast films, has been found advantageous. Polyamide or polyvinyl alcohol films have proved highly successful in this application. In addition to these films, sprayed-on silicones or waxes are also frequently employed. Although many more such examples could be cited, it is hoped that the above will show the need for abherents and their widespread use in the field of polymer processing.

Paper Coating and Pressure-Sensitive Tapes. Adhesive coated papers, cloth, and plastic films have attained great industrial importance during the last twenty years. All these materials, after being coated with adhesive and dried, have to be wound up in rolls. Abherents are needed to prevent the rolled-up adhesive coating from sticking to the backing material. These applications make very severe demands on abherents, and considerable work has been done in this field in order to develop the proper materials.

Here again, as in so many applications, the silicones have done an outstanding job. Silicone-coated papers have attained great commercial importance and are being manufactured by a large number of specialty paper manufacturers. These papers, which are coated with the silicone abherents on either one or both sides, are used as interleaving papers for various sticky substances like uncured rubber, whereas the papers

coated on one side only are used primarily as the base material for pressure-sensitive and other adhesive paper tapes. Before the introduction and acceptance of silicone coatings, wax-polyethylene coatings, straight wax coatings, and zinc stearate or talcum dusting had been used to a great extent.

An application that combines both paper coating and polymer processing provides another outlet for abherents. Polyvinyl chloride plastisols, which are dispersions of finely powdered polymer in liquid plasticizers, are frequently cast into sheets or films that are then fused into a polymeric compound. Originally, these films were cast onto stainless-steel continuous belts, an operation that entailed a considerable initial investment as well as replacement cost. These films can now be cast and fused on abherent-treated papers, and the films are peeled off the papers after fusion.

Abherent-treated papers are also used widely in the general packaging of sticky materials. These include chemicals, foods, and many others. Practically all classes of abherents are used in the packaging field.

Glass Industry. The uses of abherents in the glass industry and, more particularly, in the molding of glass, are similar in importance and application to their use in polymer processing. In glass molding, the various ingredients are melted together in large furnaces. From the melting furnace the glass melt is delivered through feeding channels, where it is cut by shears into gobs of desired size. These gobs are delivered by conveying devices to the molding stations, first to a blank mold and then to a finish mold. Subsequently, these molded bottles or other items, still very hot, are conveyed through a heated annealing furnace and are cooled slowly to release internal strains.

All metal parts coming in contact with the high-temperature glass melt have to be treated with abherents to prevent sticking of the melt to the metal. Since the glass molding industry dates back almost a hundred years, the first abherents were natural waxes and vegetable and animal oils. Later, mineral oils were used and today, silicones are employed most often. Silicones have been so very valuable in this application because of the high temperatures required in glass processing. The vaporization and carbonization of organic abherents causes fumes and crusting. The use of silicones has therefore brought about a major improvement in the speed, efficiency, and cleanliness of this operation.

Classes of Abherent Materials

WAXES

Both natural and manufactured waxes (see also Petroleum waxes) are finding application as abherents. Natural waxes that have gained importance in this field are paraffin and microcrystalline waxes (both types are petroleum products); waxes of vegetable origin, such as carnauba or candelilla wax; and waxes of animal origin, such as spermaceti.

The petroleum-based waxes have the disadvantage of relatively low melting points, which may produce stickiness near the melting point, rather than release. These waxes also are subject to oxidation at high temperatures. The vegetable waxes, like carnauba wax, are excellent abherents but, being natural products, have the disadvantage of variation in color and price. High price also has been limiting the use of spermaceti wax.

Synthetic or manufactured waxes have attained greater importance for use as abherents. Practically all aliphatic alcohols from the C-10 up have found use as

abherents. The same can be said about fatty acids above C-12. The fatty acid having attained the widest use as an abherent is stearic acid, which is available highly purified at a reasonable price. It has a sharply defined melting point and good wetting properties. Since stearic acid also has a very limited compatibility with organic polymers, it has been found an efficient abherent in a great number of applications. As examples, one may mention the internal lubrication produced (by addition to the formulation) in polyvinyl chloride and styrene polymers and copolymers. The use of stearic acid in rubber compounds, where it not only serves as an abherent but performs other functions as well, has been covered previously.

The glyceryl stearates and various glycol stearates comprise another group of synthetic waxes that are employed as abherents in a multitude of applications. Two important members of this family are (1) glyceryl monostearate (α -stearin), used as an additive in polyvinyl chloride compounds for the manufacture of sheeting and film, and as an additive in polybutenes (Vistanex), which otherwise have exceptional adhesive properties, and (2) diethylene glycol monostearate, used as an incorporated abherent in rubber processing and in polyvinyl chloride compounds and as an abherent coating on paper. Another interesting group in this family of glyceryl fatty acid esters are the hydrogenated oils. Of particular industrial interest is fully hydrogenated castor oil, which is sold under the trade name of Opalwax. Chemically, Opalwax is glyceryl tri(hydroxystearate). This wax has an exceptionally high melting point and is used as an abherent in rubber compounds, coated fabrics, and papers. Probably the most important single abherent in the family of synthetic waxes, known under various trade names (Acrawax C, Advawax 280), is reported to consist primarily of ethylene bis-stearamide. This is an amorphous wax of good color, excellent heat stability and a melting point of 140–143°C, probably the highest of all the waxes. This wax, having such a high melting point, can be obtained and shipped in a very finely pulverized form, which makes it more convenient to apply than most waxes. It also has extremely limited solubility and compatibility and, therefore, can be used in a great number of systems. Acrawax C has been found useful as an abherent in almost all types of polymer processing and, in many cases, acts in the finished polymer film or sheet as an antiblocking agent, or slip agent, preventing adhesion of two layers of film to each other. This wax has also found many uses as a release agent in metal processing.

METAL SALTS OF FATTY ACIDS

The metal salts of fatty acids and primarily of stearic acid (see Driers and metallic soaps) have acquired an important industrial position as abherents. As high-melting solids usually available in a powdered form, these metal salts are applied primarily as dusts, but also in many cases are incorporated into polymeric compounds as internal abherents or release agents. In rare instances water dispersions of these metallic salts have also been applied. Zinc stearate, for example, is available in a water dispersion and has been used in this form in rubber processing. The most important metallic salts used as abherents are calcium stearate, zinc stearate, lead stearate, magnesium stearate, and aluminum stearate. Which metallic salt is chosen for a specific application depends primarily on the polymers and other surfaces involved. Calcium and lead stearate are the dominant abherents in polyvinyl chloride processing, where both also have heat stabilizing effects. Zinc stearate is substituted for lead stearate in specific cases where nontoxicity is a requirement, but it does not have anywhere near

the stabilizing effect of lead stearate. Calcium stearate is probably the most effective abherent in polyvinyl chloride.

As an abherent in polystyrene, zinc stearate has found the greatest use. Aluminum stearate is also effective with many polymers. In the field of rubber processing, aluminum and magnesium salts are the preferred abherents. Zinc and aluminum stearates have found widespread use in metal processing, particularly in the drawing of wire, in sheet-metal stamping, and in powder metallurgy. The reasons for the superior functioning of one metallic salt over another in various applications have been determined empirically. Frequently the choice of the right stearate can be based on melting point, insolubility, and particle size to which the stearate can be ground or precipitated.

Metallic salts are used indirectly as abherents where a low-melting wax is the primary abherent and the metallic salt is employed to increase the melting point of the mixture. Thus, blends of aluminum stearate and paraffin wax and also of zinc stearate and stearic acid have been made in order to adjust melting points and physical properties of the primary abherent.

POLYMERIC ABHERENTS

Polyvinyl Alcohol. (See Vinyl compounds.) This polymer, which is completely water-soluble and incompatible with practically all organic polymers, has found a variety of uses as an abherent. It is applied as a coating from a water solution, or in the form of a cast or extruded film. One of the major applications is in the molding or lay-up forming of polyesters and epoxides.

Polyamides (qv). Since polyamides are insoluble in most of the commonly used solvents, they find application only in the form of extruded films. These are used with polyester and epoxide lay-ups and are draped over the metal or plaster mold in order to effect release of the cured formed shape from the pattern.

Polyethylene. (See Olefin polymers.) This polymer is used as an abherent film (in the form of extruded tubular or flat film) in the processing and shipping of uncured rubber, and as a paper laminate in the packaging of sticky materials.

Silicones (qv). Silicones represent the most important class of abherents despite their rather recent origin. The generic name "silicones" is applied to a wide range of compounds consisting of silicon-oxygen chains with carbon-containing side groups, such as methyl, ethyl, or phenyl, attached directly to the silica. The commercially useful silicone abherents are all polymeric in order to obtain high boiling points and, therefore, low volatilities at room temperature, heat resistance, and resistance to oxidation. The higher the molecular weight, the greater the chemical resistance and, of course, also the viscosity.

No statistics are available as yet to show the tremendous importance of silicones (in various forms) as abherents, but it is clear that they have replaced other, conventional, products to a very great extent. Prices of the silicones are in the range of about 10 times the cost of conventional abherents, yet in actual use they are in many cases considerably cheaper, because of the very small amounts needed (often they are used in highly diluted solutions or water dispersions below 1% silicone content), and also because they do not build up on metal surfaces as metal stearates do. As a result, they save considerable time in the cleaning of molds or metal casting forms. In the field of polymer processing the only word of warning that applies to the use of silicones is that their abherent properties are too good. In many cases, where surface treat-

ments in the form of printing inks or adhesives have to be applied later, the silicones will interfere with adhesion.

The silicones are used in three forms: fluids, resins, and greases.

Silicone Fluids. Commercially, the most important group of fluid abherents are based on dimethyl silicone. They can be applied either full strength or in solution, or in a water emulsion. These silicone fluids have almost every property required of an ideal abherent:

1. Excellent heat resistance and stability.
2. Low surface tension.
3. Great chemical inertness, especially toward organic materials and polymers.
4. Colorless appearance and nonstaining qualities.
5. Physiological inertness.

Their outstanding properties, together with the ease with which they can be applied, make the silicones ideal abherents in many instances. In applications such as metal processing and glass molding, where extremely high temperatures are involved, the silicones actually are the only abherents that will allow continuous use with great ease.

Silicone Resins. These are cured by heat and catalysts which usually are metallic salts or organic amines. They cure by a condensation reaction in which, by removal of water, oxygen bridges are formed between chains. The more crosslinking occurs, the harder the resin coatings will be. Crosslinking, of course, is favored by a higher functionality of the basic building block. Whereas the silicone fluids usually possess two carbon-containing groups to each Si in the chain, the base groups for resins usually contain only one carbon group for each silica, the rest being hydroxyls.

Silicone resins are manufactured and sold in solution in organic solvents since the solution increases their shelf life. They can be applied by spraying, dipping, or brushing. They are used as abherents primarily on metal surfaces and have found their most important application in baking pans in commercial bakeries. Here again the importance of the silicone resin coating lies in the extreme heat resistance of the fully cured films, which can be used up to approximately 400°F. A paint formulated from silicone resin with powdered aluminum pigment can attain heat resistance up to 500°F.

Silicone Greases. These are silicone fluids thickened with either lithium octoate or with a silica gel, such as Cab-o-sil. The greases have the advantage of not running off too easily, even at elevated temperatures, and therefore acquiring somewhat more permanence than a silicone fluid would when applied to metal or other surfaces.

Fluorocarbon Polymers. The fluorocarbon polymers (see Resins containing fluorine) also are a relatively new group of materials used in many forms. They can be formed into sheets, rods, and other shapes. The fluorocarbon polymers are also available in water dispersions, but their general use as abherents has been retarded by their very high cost.

They do have the properties required of good abherents, namely, very high chemical inertness and high heat resistance. They are employed as abherents in the form of films and sheets, primarily where permanent gasketing between two sticky surfaces is required. Their use, of course, is very limited since a fluorocarbon film or sheet sells for well above \$10.00 per pound. One application of polytetrafluoroethylene, as mentioned previously, is as a coating for metal frying pans for home use. This coating is applied as a dispersion, which is dried and fused at approximately 250°C.

INORGANICS

Inorganics are the oldest abherents known. Owing to their insolubility they are used strictly in the form of powders, which exert abherent properties generally because of their flake-like crystal structure. The most important representatives of this class of abherents are talcum (see Talc) and mica (qv). These are always applied as a fine powder sprayed or dusted onto a surface to prevent adhesion between that surface and metal or similar surfaces. They are frequently blended with metal stearates to improve their abherent action. A major application for these inorganic abherents is the dusting of soft rubber products, ie, tubing, rubber bands, and soft rubber sheets. Another example for the use of talcum as an abherent is the dusting of freshly printed paper or polymeric film in order to be able to wind these materials into rolls before the inks are completely dried, without transferring the inks to the backs of the web in the roll.

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ABIETIC ACID, $C_{19}H_{29}COOH$. See Rosin and rosin derivatives; Terpenes and terpenoids.

ABLATION

The word ablation, in the sense used in this article, has been applied for many years by astronomers and astrophysicists to describe the erosion and disintegration of meteors entering the atmosphere of the earth. The familiar, transient, incandescent trails, called shooting stars, are evidence of the intense heat generated by the interaction of these high-velocity particles with the atmosphere. Most meteors are completely vaporized or otherwise disintegrated before they reach the surface of the earth. A few, called meteorites, do reach the surface because of their large initial size, favorable composition, and trajectory. These can be seen to be severely eroded or ablated and very likely fragmented.

Ablation has recently acquired technological significance in the development of long-range missiles which travel outside of the atmosphere and must reenter in the target area. Recoverable earth satellites, lunar and interplanetary vehicles, as well as long-range missiles, can thus be regarded as man-made meteorites. For a number of current missions involving reentry, it has been found to be most practical to insure the survival of the vehicle by covering its surface with materials that erode or ablate slowly and smoothly in such a manner as to protect the payload and structure from damage. The development and study of materials for this ablation application constitute an important new area of chemical technology.

The reentry problem has been the main field of application of ablation, and a large number of detailed studies have been published; other applications include the protection of rocket nozzle structures from attrition by hot propellant gases and the insulation of rocket motor case structures from the heat from the burning propellant.

In retrospect, ablation is not an altogether novel technical phenomenon. In electric furnaces or in carbon-arc light sources, electrodes are continuously fed into the hot zone of the device and could be said to ablate. In nature, it is likely that the longevity of redwood and sequoia trees is due in part to the protection of their vital parts from fire damage by the unique thickness and ablating properties of their bark.

In very hot environments any material will ablate. The details of the process and the rates at which ablation occurs, however, depend on both the nature of the material and the nature of the environment. In a steady environment, which is not usually encountered in practice, the response of the material often includes a transient phase and a quasi-steady state. For example, if one surface of a large slab of solid metal is exposed to a very hot stream of chemically inert gas, its surface temperature will rise at a rate which depends on the difference between the rate at which heat reaches the surface from the hot environment and the rate at which heat is conducted into the material. After a finite time and at a temperature which is a characteristic of the metal, surface melting will occur and hot liquid may begin to drip or be blown off the surface. After this, the face of the solid will recede or ablate at a steady rate which depends on the latent heat of melting of the metal, its heat capacity, and its thermal conductivity.

If the same experiment were done with a slab of material which sublimates instead of melting, rather similar transient heating and quasi-steady ablation would be expected. However, the ejection of vapor from the surface would interfere with the convective transfer of heat from the gas stream to the surface. This effect has been called "blocking action" and is due to the thickening of the boundary layer and the alteration of the temperature gradient at the surface. In many practical situations blocking action reduces the net transport of heat from the gas stream to the solid by more than 50%.

The materials that have been found most useful for ablating heat protection systems for reentry vehicles and rocket nozzles usually do not merely melt or sublime in response to heating, but, rather, decompose to give large volumes of gas and leave a porous refractory residue. A typical material is a composite of nylon fibers and phenolic resin. When a slab of this material is exposed to the stream of hot gas, two distinct, consecutive, transient processes precede the development of a quasi-steady state. In the first, the surface temperature rises to the decomposition temperature of the composite which then begins to char or carbonize and evolve rather low-molecular-weight gases. Then, only the interface between the char layer and the virgin material moves into the slab. During this period, gases generated in the course of the char-forming process at the moving interface diffuse through the char and absorb heat. These heated gases are then ejected into the boundary layer to exert a blocking action.

As the char layer thickens, the amount of heat reaching the moving interface is reduced by the insulating effect of the porous char combined with the cooling effect of the diffusing gases. Thus the rate of decomposition and gas formation at the interface is also reduced. As a result the surface temperature of the char rises until it begins to ablate. This second transient, the development of the char layer, terminates when

the rate of char-surface ablation equals the rate of recession of the char-virgin material interface. The combined effect of the heat exchange in the porous char and the blocking action is often called "transpiration cooling." This cooling effect can reduce the net heat load on the remaining virgin plastic, which is a rather good thermal insulator, to a very small fraction of what it would otherwise be.

The fact that the porous residue generated in the decomposition of the virgin, phenolic-nylon composite is carbon makes it possible for a hot surface to be presented to the environment. This not only can reduce the driving temperature gradient across the gaseous boundary layer, but also can radiate back into the environment a substantial amount of the energy that it receives.

In order to complete this introductory and qualitative description of ablation it is necessary to point out that chemical reactions between the environmental gas and the ablating material can usually be expected, and the erosion of the hot surface need not be solely thermal or chemical. Surface removal can also be due to shear forces generated by the flowing environmental gas, pressure forces from the gas generated at the char-virgin material interface, or thermal stresses caused by the temperature gradients in the solid material.

In addition, the usefulness of an ablating material does not depend altogether on its rate of ablation, but rather on its net ability to prevent heat from the environment from damaging the structure or payload on which it is applied. Thus, the sensitivity of the payload is an additional factor in ablation design. Other requirements for specific electrical and mechanical properties often arise.

The Ablation Environment

In the practical situations where ablating heat protection systems are applied, the environments are quite diverse and the interactions among the effects of surface temperature, transpiration cooling, radiation, and insulation depend as much on the nature of the environment as they do on the nature of the material. The reentry environments, or more generally the environments generated at the surface of any body flying through the atmosphere at hypersonic velocities, deserve further discussion at this point not only because of their influence on material performance, but also because they can be more severe and are otherwise quite different from any of the familiar hot environments encountered in other technologies.

Near the leading point or points (stagnation points) of a hypervelocity vehicle flying through an atmosphere, the gas molecules are abruptly accelerated to the velocity of the vehicle. The translational energy imparted to the gas, after it has been partitioned among the various molecular and atomic degrees of freedom that are available, then appears as a temperature rise to the stagnation temperature. The actual temperature change, however, is not directly related to the velocity because the relationships between energy content and temperature depend on the extent to which dissociations or other endothermic processes have taken place and this, even at equilibrium, in turn depends on pressure. Since the energy content of the environment is more directly related to the velocity of the vehicle than the temperature, the former is frequently used in discussions and calculations. Moreover, the energy content is independent of whether the energy partition is complete or not—that is, whether the gas is in true thermal equilibrium.

The gross heating rate on the body depends on its velocity. The velocity determines the specific energy content of the gas approximately according to the relationship

$$H_s = \frac{V^2}{2J}$$

where H_s is the stagnation energy content or enthalpy per unit weight, V is the velocity of the vehicle, and J is the mechanical equivalent of heat. The gross heating rate also depends on the local pressure, which is determined by the body velocity; on the ambient pressure, which, of course, depends on the altitude; and on the point on the body that is being considered. The local pressure is highest at the leading points of the body. It is lowest on trailing surfaces of the body, and in between depends on the angle of the surface to the flight path and other details of the configuration. As in other problems involving convective heat transfer, the question of whether the flow is laminar or turbulent also influences the effective boundary layer thickness and must be taken into account. Turbulent heating can be much more severe than the calculated laminar heating.

Since the transient responses of materials play such an important part in the ablation phenomena, the time of heating is quite as important as the heating rate. The time of heating and the heating rate are related in a ballistic reentry trajectory—that is, the trajectory of an unpowered, axisymmetric body. The relationship depends on the angle of the flight path to the local horizontal. When this angle is small, the deceleration of the body occurs at high altitudes where the pressure is low and the heating rate is correspondingly low. The rate of deceleration is also low (an important consideration in manned flights), so that the time required to reach velocities at which the heating is insignificant is long.

When the flight path makes a large angle with the horizontal, much of the deceleration occurs at lower altitudes and much more rapidly. In fact, the deceleration of a reentering intercontinental-range missile can be comparable to that suffered by an automobile hitting a solid brick wall at 60 miles per hour. Under these conditions the heating rate is much higher because the ambient pressures are higher, but the time of heating is much shorter.

For a given path angle, the altitude at which deceleration takes place depends on the weight and bluntness of the body. A light blunt body (low ratio of weight to drag) can be expected to decelerate at a higher altitude than a heavy pointed body (high ratio of weight to drag). It turns out that the rates of deceleration are relatively independent of the weight-to-drag ratio, but the heating rates are very responsive to this ratio. This is true not only because of the pressure (altitude) effect on heat transfer, but also because of the entropy changes in the flow which depend on body configuration.

The detailed flight mechanics, aerodynamics, and aerothermochemistry associated with reentry are outside of the scope of this article. However, some typical reentry trajectories and heating rates are shown in Figure 1. The ordinate of this graph is altitude, in thousands of feet. The altitude determines the gas density near the body. The abscissa is shown as velocity and also as stagnation gas enthalpy (also as stagnation gas temperature for a particular altitude, in this case 70,000 ft). The lettered curves show the relationship of velocity to altitude for representative reentry trajectories. The numbered curves are lines of equal heating rate; the heating rates

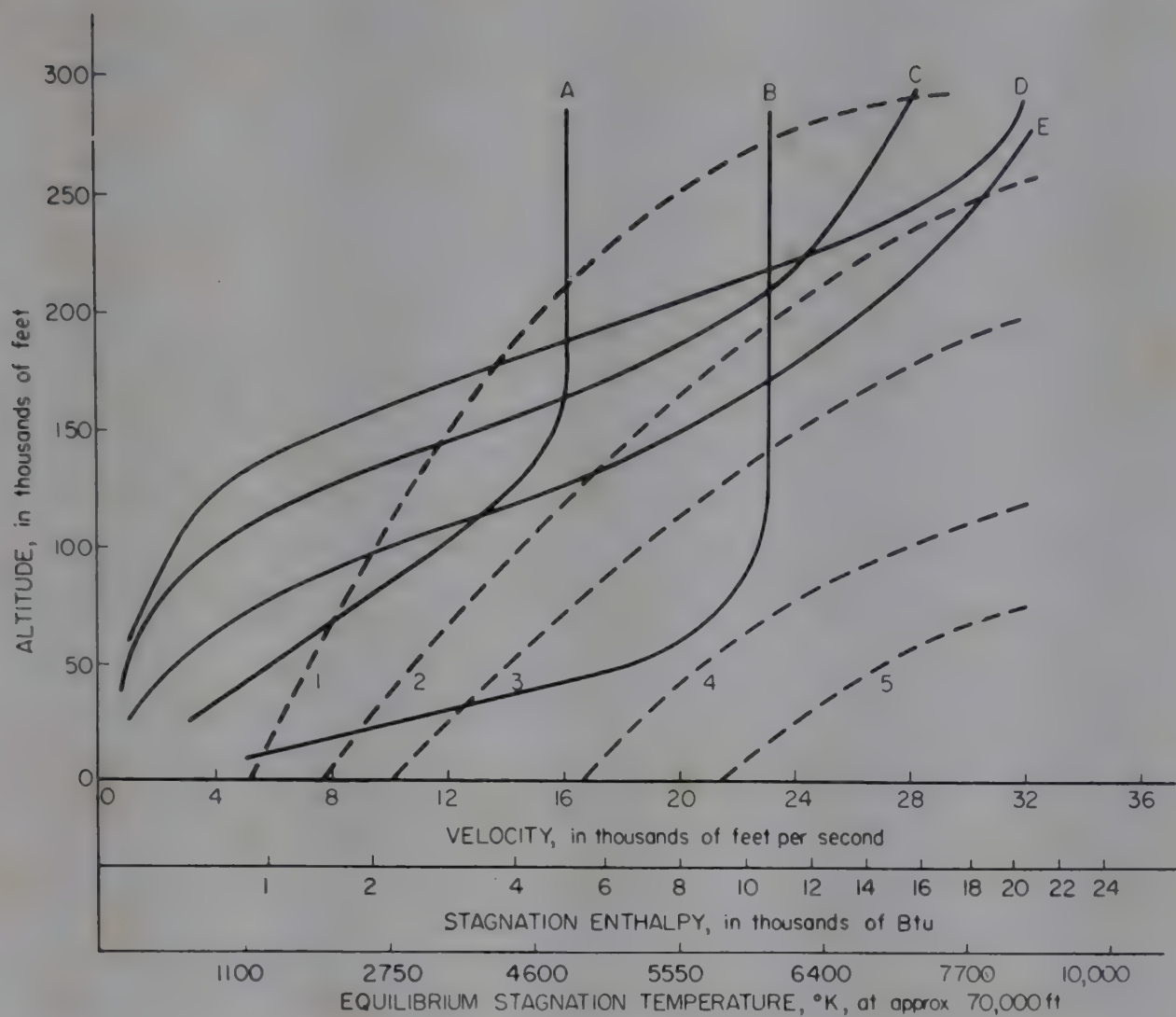


Fig. 1. Hypervelocity flight environments (7). Curve A, intermediate-range nose cone; B, intercontinental-range nose cone; C, manned orbital vehicle; D, satellite; and E, space probe. The heating rates (calculated for laminar flow about a body with a nose radius of 6 in.) and corresponding radiation equilibrium temperatures (calculated for an emissivity of 0.9) for each numbered curve are as follows:

Curve	Heating rate, Btu/(ft ²)(sec)	Radiation equilibrium temperature	
		°F	°K
1	50	2,830	1,828
2	200	4,200	2,589
3	500	5,400	3,255
4	2,000	7,800	4,589
5	5,000	10,000	5,811

shown are those calculated for laminar heating of a 6-inch nose radius. Notice that the highest heating rates occur for trajectories which combine high velocities and low altitudes. On the other hand, a vehicle which decelerates at a very high altitude is not subject to such severe heating. The temperature at which the vehicle surface would be in radiation equilibrium with the environment if its emissivity were 0.9 for each heat rate (each numbered curve) is given in the legend to Figure 1. These temperatures are perhaps more relevant than the gas temperatures shown on the abscissa.

As the flight path angles and body configurations change, the trajectories and heating rates can vary from those shown in Figure 1. However, the figure does provide some orientation as to the velocities and heating rates that are likely to be encountered and how they may vary from mission to mission. The heating times can

vary from 20 to 30 seconds for the steep trajectory of a long-range-weapon vehicle to more than a 1000 seconds for a manned return from the moon. For maneuverable vehicles or simply vehicles with lift, these times can be even greater.

The rocket nozzle environments in which ablating materials are used are also rather complicated. The exhaust gas compositions are different from those at the nose of a flight vehicle, and the configurations are often closed so that heat loss by radiation is likely to be less important. Since the rocket gases are products of combustion and derive their energy from chemical reactions, their temperatures are limited by the reversibility of the combustion reactions. The heating rates and heating times, and the necessity for dimensional stability make the requirements for rocket nozzles different but no less severe than those for reentry nose cones.

The diversity of the environments in which ablating materials are expected to perform suggests that there is not likely to be one material which is best for all applications. At the relatively low heating loads associated with certain manned reentry missions from space, even though the enthalpy levels and temperatures in the gas are very high, the outside surface temperature of the skin material cannot be driven above that at which radiation equilibrium is established. This temperature can be in a range where the char or other surface material is quite stable, and the quasi-steady state of ablation is never achieved. The amount of heat reaching the structure or payload would then be determined largely by the effective thermal conductivity of the ablation material. Actual attrition of the surface would be relatively unimportant.

At the relatively high heating loads associated with missile reentry, no materials are stable. The quasi-steady state may be reached in a few seconds and the protective action of the ablation material then depends on the effectiveness with which transpiration cooling reduces the rate of attrition of the surface. Conductivity can be relatively less important in this application because surface recession can keep up with the heat pulse into the material.

The foregoing discussion has dealt particularly with the stagnation regions of the vehicles. Lee surfaces of missile vehicles may require treatment similar to that for stagnation points of manned vehicles so that, in general, it may be desirable not only to use different materials on different vehicles, but different materials on different parts of the same vehicle.

Somewhat the same applies to rocket nozzle materials. At the constricted part of the nozzle, the throat, heating rates are higher than they are downstream on the skirt where the flow is expanded and the pressure is lower. As would be expected, different ablation materials are used on the throat and on the skirt.

Laboratory Studies of Ablation

Direct studies of ablation during reentry or full-scale tests of rocket motors are unreasonably costly and inconvenient for the systematic study of large numbers of potentially useful ablation materials. A great deal of effort has been devoted, therefore, to the development of laboratory simulations of the relevant environments. Diverse chemical flames, solar furnaces, pebble-bed gas heaters, and electric-arc devices have been used as heat sources. For simulating flow conditions, the heaters are used in conjunction with wind tunnels of various kinds. Shock tubes can generate high-velocity gases and are useful in aerodynamic studies; in general, however, they are not useful for testing materials because the flow duration is inadequate.

Complete simulation of the reentry environment or understanding of the scaling factors required in interpreting rocket nozzle tests have as yet not been achieved. However, certain types of electric-arc heaters or plasma generators have been most useful because the temperatures and heat-transfer rates that are relevant are often inaccessible with other devices; because the composition of the hot gas can be controlled better than with other types of heaters; and finally because they can be adapted to heating gas for wind tunnel operation. Even with incomplete simulation, a great many useful inferences about the performance of an ablation material have been made by correlation of laboratory results with flight-test data and with analytical studies of the physics of ablation.

Ablative Materials. Some of the earliest test results have shown that ablation rate cannot, in general, be correlated with high-temperature stability. Table 1 shows, for example, that in a particular hot gaseous environment, refractory zirconia ablates sixteen times as rapidly as a relatively unstable organic plastic.

Table 1. Relative Durability of Materials Exposed to Heating in a Water-Stabilized Arc (10).
(Gas temperature 7000°C; heating rate 2000 Btu/(ft²)(sec); time 10 sec)

Material	Relative weight loss
graphite	1.0
nylon-phenolic	1.48
silicon carbide	2.1-7.8
silica-phenolic	2.7
glass-phenolic	2.7
silica	2.9
alumina	8.5-17.0
mullite	10
zirconia	16
copper	75

The dependence of relative ablation rates on the nature of the environment is shown in Table 2. The relative erosion rates of phenolic resin compounded with glass fibers, silica fibers, and nylon fibers are strongly dependent on the conditions of exposure. Under the least severe conditions, a hot gas wind tunnel, glass and silica fiber composites are about equivalent and almost five times more durable than the nylon fiber composite.

Table 2. Relative Erosion Rates of Various Materials at Different Temperatures of Exposure (11)

Material	Resin, %	Erosion rates at °C ^a		
		1800	2500	7000
phenolic-glass cloth	27	1.0	2.7	2.5
	37	1.2	2.5	2.0
	44	1.6	2.2	2.0
	65	1.7	1.5	1.4
phenolic-silica cloth	41	1.4	1.0	2.1
phenolic-nylon cloth	57	4.7	2.5	1.0

^a Comparison of ratings should be made only within columns. No connection among the data at the different temperatures is intended.

At the intermediate condition (which corresponds to the conditions generated by an alcohol-oxygen rocket motor), the silica composite is most effective, and almost three times better than glass or nylon. The most severe condition generated by a plasma torch showed nylon best and about twice as good as glass or silica.

The results of these experiments were rationalized using the data in Table 3 in which the heat absorbing capacities—that is, the integrated specific heat including latent heats from room temperature to 5000°K—and the relative volume of gas generated at 5000°K for various substances are tabulated. It may be seen in Table 3 that if various materials are heated to 5000°K in an equilibrium process, organic materials would absorb much more heat than silica, or indeed any other solid in the list. In addition, the heating of the organic plastic produces more gas, which might further impede the transfer of heat to the body.

Table 3. Estimate of Integrated Specific Heats from 300–5000°K and Equilibrium Volume of Gas Generated per Gram at 5000°K for Various Substances (11)

Substance	Heat absorbed, cal/g	Relative gas volume
H ₂ (gas)	67,000	1.0
(CH ₂) _n (organic plastic)	24,000	0.21
(CH) _n (organic plastic)	20,000	0.15
C (graphite)	16,670	0.08
(C ₆ H ₁₂ O ₆) _n (cellulose)	5,760	0.10
BeO (beryllia)	7,080	0.08
MgO (magnesia)	5,500	0.05
SiO ₂ (silica)	2,800	0.05
Be (beryllium)	9,876	0.11
Cu (copper)	1,600	0.016
(C ₂ F ₄) _n (Teflon)	6,300	0.06
H ₂ O (water)	14,500	0.16
He (helium)	3,525	0.25

These data account for the relatively high performance of the all-organic material in the 7000°C environment (Table 2). In the 2500°C environment the relatively high softening point of the silica fiber gives it an advantage. In the 1800°C environment the extra refractory character of silica as compared with glass is not an advantage.

The thermal erosion rates of organic plastics do not depend on their empirical composition alone. Plastics which form cokelike char on their surface in response to heating tend to erode more slowly. This is altogether to be expected because of the high temperature that can be sustained by a carbon surface which tends to reduce the driving gradients and increase the reradiation from the surface. In addition, a plastic which gives a high yield of carbon on pyrolysis also gives a high yield of hydrogen or other low-molecular-weight gases which are most effective in reducing the net heat transfer to the surface. Among the common plastics the phenolic resins give the highest yield of coke on pyrolysis. This probably accounts for their wide use in the formulation of organic ablating materials.

As pointed out above, in the practical application of ablation the recession of the surface is not always a uniquely thermal effect. Shear forces generated by the flow of environmental gas, pressures generated by the decomposition or volatilization of the material, and thermal stresses can contribute to the removal of material. For this reason plastics reinforced with strong refractory fibers are often selected. For the

same reasons, inorganic materials such as silica, which give a melt of high viscosity, ablate at a lower rate than alumina, which has a higher melting point but gives a less viscous liquid phase.

When composites of inorganic refractory materials with organic resins are used, the geometry of the composite can be important. Particles of granular inorganic materials which have higher thermal conductivities than the usual organic resin matrix can be blown out of the matrix by gases generated on their back interfaces. Fibrous refractories with their long axes in the plane of the surface can be lost in a similar fashion as the matrix material degrades on the back interfaces. Fibers normal to the surface eliminate this problem and can contribute to holding the char on the surface. These, however, give composites of the highest thermal conductivity. As a practical matter, obliquely oriented refractory fibers and fabrics which are "shingled" downstream to the flow are frequently used when shear forces are prominent.

Among the inorganic fibers which are useful in ablative composites are glass, leached glass (see Glass), carbon, and varieties of asbestos. For the highest temperature environments and the highest heating rates and when shear forces are low, organic fibers such as nylon are used advantageously in the ablative composites (see Table 2). One of the considerations in the selection of an organic fiber filler is the temperature at which it starts to generate gas. If gas is generated before the matrix material is sufficiently degraded and porous to prevent pressure buildup in the composite, premature failure can be expected unless other provisions are made for venting.

For some applications, such as antenna covers, the presence of an electrically conductive char on the surface of the ablation material could be undesirable. In other applications it might be desirable to avoid generating a high temperature on the ablating surface. In both of these cases, polytetrafluoroethylene and other compositions that do not char have been found useful. When the heating rate is relatively low and the heating time is long, as might occur in a manned reentry trajectory (which must be kept flat to minimize deceleration loads), the insulating capability of the material may be as important as its heat absorbing performance. Under these conditions, low-density compositions which are foamed or contain preformed bubbles can be used.

Graphite and baked carbon (see Carbon) have also been considered as ablation materials where it is desired to preserve the original shape or dimensions of a vehicle. At high speeds the ablation of graphite is likely to be due to chemical action—that is, oxidation, rather than thermal effects. This argument is presumably applicable to the chars that form on organic resins. The use of refractory ablating materials such as carbon leads to the possibility of thermal shock failure. At the relevant high heating rates, steep temperature gradients may be generated and the accompanying thermal stresses can exceed the load-bearing capability of the material. Refractory ablating materials tend to have higher thermal conductivities than organic types, so that special insulation may be required to keep the back wall temperature within tolerable limits. The high coefficients of thermal expansion of organic materials may require that special attention be given to the structural compatibility of the ablation material with the rest of the vehicle structure. This is particularly true when the entire vehicle is subject to a wide range of temperatures in transportation, storage, or orbit.

The composition of many ablating materials is regarded as proprietary or is described only in the classified literature. For example, special castable organic compositions have been used by the General Electric Company. An inorganic com-

posite in which a refractory powder is sintered into a refractory metal honeycomb has been used by the AVCO Corporation. Silicones, epoxy resins, filled polyethylene, and many other types of material have also been studied.

Design Considerations

The decision to use a particular ablating system for a particular task must be based on considerations of weight and of cost in time or money compared to competitive heat protection systems (which may or may not make use of ablation). This means that a rational basis for estimating weights and costs must be available. Costs are determined by the design effort required as well as the raw materials and fabrication. These will vary from one establishment to another depending on the experience and facilities that are available. In general, materials that can be cast to final dimensions are likely to be preferable to those that require elaborate molding, pressing, and machining. Saving in system weight can also be assigned a dollar value, and appropriate trade offs can then be made.

A number of analytical schemes have been proposed for defining the nature and thickness of the ablating material required for a particular reentry vehicle. For inputs, these schemes depend on the trajectory, configuration, tolerable structural temperature, and heat capacity, as well as ablating material characteristics. As expected for charring plastics, these schemes require the continuous and simultaneous solution of the equations for transient heat conduction through the char and virgin plastic, taking into account transpiration cooling, back radiation, chemical reactions with the environment, the char-forming process, and the char-removal process.

At present the extent of our knowledge does not permit the selection of a material and the design of a thermal shield from first principles. (This is equally true in other much more mature technologies.) However, these schemes do provide a rational basis for making the best use of empirical data.

Among the more or less traditional chemical methods that have been particularly useful in the study of the ablation of plastics is thermogravimetric analysis. In this procedure the weight changes that occur in a sample of the plastic as the temperature is raised are continuously observed. Using these data and data on the composition of the evolved gases, the empirical equations for the kinetics of char formation that are required for the overall ablation analysis can be constructed. The gas compositions are also required for the evaluation of the transpiration cooling effects.

The relationships among the porosity and other properties of the char and the characteristics of the virgin material also present chemical problems of challenging complexity. In some respects these problems are similar to those encountered in the manufacture of coke. On the basis of previous experience with chemical problems bearing some similarity, complicated interactions among the constituents of composite materials can be expected. For example, an inorganic filler can affect the kinetics of the decomposition of an organic resin by changing the effective thermal conductivity, as well as by specific, chemical, catalytic effects.

Conclusions

In the few years that ablation has been studied, the whole complexion of the heat protection problem has been changed. Yet the development of ablation materials is still in its infancy. When one compares the theoretically possible heat-diversion

capabilities of material with those that have been achieved, improvement factors of ten or twenty appear possible. Some of the directions that current development work is taking have been indicated above, implicitly at least; these approaches depend on performance objectives.

With the further evolution of higher speed airplanes, and perhaps also of nuclear technology, ablation materials may be used in volume as expendable elements in much the same way that chemical fuels are used today. Whether large-volume applications develop or not, the general technology that has developed around the ablation problem can certainly be expected to find further application.

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ABRASIVES

Abrasives are of immense importance in a wide variety of industries. They are used in three forms: (1) attached to flat, flexible surfaces, such as paper or cloth, (2) bonded into a solid body, such as a grinding wheel, or (3) applied in a loose, granular or powdered form.

Abrading, or more commonly, grinding, was known and used as long as 20,000 to 25,000 years ago. There is archaeological evidence that ancient man used rough stones to shape horn or bone into useful instruments. As early as 1500 BC, sandstone was used to sharpen knives in Egypt. Pliny the Elder mentions the use of emery in the first century AD, and Leonardo da Vinci, in the fourteenth century, left designs for machines to perform internal grinding and drawings of wheels for grinding, polishing, and buffing. In 1608 the Indian Chief Powhatan, in order to recompense himself for the boldness of his daughter Pocahontas in saving the life of the condemned Captain John Smith, ordered the Captain to go to Jamestown and procure for him "two great guns and a grindstone."

Man-made grinding wheels were first reported in 1825, manufactured of natural corundum and gummed resin by the Hindus. In 1857, a rubber-bonded wheel was patented and the patent literature of that time also shows sodium silicate and ceramic-bonded wheels using natural emery or corundum as the abrasive.

In 1873, Franklin B. Norton, owner of a small pottery shop in Worcester, Mass., was discussing grinding wheels with one of his employees, Sven Pulson. Mr. Pulson wagered with Mr. Norton that within three tries he could produce a solid emery wheel by mixing emery and clay and by burning the formed mixture in the regular pottery kiln. The loser was to finance a gallon of beer. The first wheel was made with slip clay as the bond and was fired on top of an inverted flower pot, but when the kiln was drawn the wheel had run down over the sides of the flower pot. On the next firing, the wheel was blistered, but the third wheel was perfect and Norton paid the bet (1).

In 1876, Franklin Norton applied for a patent on the emery and slip clay-bonded wheel. This invention led to the formation of the Norton Emery Wheel Company, later the Norton Company. Today this company is the largest producer of abrasive products in the world.

Edward G. Acheson discovered silicon carbide in 1891 and Charles B. Jacobs found a method of producing artificial aluminum oxide in 1899. These two products, coupled with Dr. Leo Baekeland's invention of phenolic resin in 1907 and Franklin Norton's slip clay-vitrified bond, set the stage for the growth of abrasives into the more than \$415,000,000 industry it is today (2).

Measurement of Abrasiveness

The means by which the abrasive action of a substance can be measured is, of necessity, relative. The act of abrading implies that something will be abraded and the measure of the efficiency with which the abrasive action is performed must, therefore, be stated in terms comparing it to another substance, more or less abrasive than itself. Abrasiveness can be defined by four properties: *hardness*, *toughness*, degree of *chemical inertness* and, in some instances, *resistance to heat conduction*.

While it would seem that optimum characteristics in each of these categories would define the ultimate abrasive, in practice lesser combinations may sometimes be more

Table 1. Scales of Hardness

Mohs' scale		Ridgway's extension of Mohs' scale (3)		Knoop hardness numbers, at a 100g-load (K-100) average (4)	
talc	1				
gypsum	2				
calcite	3				
fluorite	4				
apatite	5				
feldspar	6	orthoclase or periclase	6		
quartz	7	vitreous pure silica	7	tool steel Rc (Rockwell c) 60.5	740
topaz	8	quartz	8	quartz	820
corundum	9	topaz	9	topaz	1340
diamond	10	garnet	10	garnet	1360
		fused zirconia	11	tungsten carbide	1880
		fused alumina	12	fused alumina	2050
		silicon carbide	13	silicon carbide	2460
		boron carbide	14	boron carbide	2760
		diamond	15	diamond	8350

desirable. Although the measurement of the aforementioned properties defines this characteristic, it should be recognized that a low as well as a high degree of abrasiveness can make a compound ideally suited for abrading.

Hardness (qv) (20). The earliest scale of hardness still in extensive use is that of Mohs. It was introduced by Friedrich Mohs, a German mineralogist, about one century ago, and is based on the relative hardness of minerals, the one which would scratch or mark another being considered the harder. Mohs' scale is unsatisfactory for modern abrasives because from the softest, 1, to the hardest, 10, the scale is not linear (ie, a hardness of 2 is not twice as hard as a hardness of 1, a hardness of 9 is not three times as hard as a hardness of 3, etc) and because most satisfactory abrasives lie between 9 and 10 and are not easily differentiated by the scale (see Table 1).

The Knoop scale of hardness is the most widely used means of establishing hardness of very hard materials (see Table 1). It is based on resistance to penetration by another material. Thus, a specially shaped diamond point is forced into the test material, and the indentation and the load required to produce it are measured. Knoop's scale is usually given in terms of kilograms of load per square millimeter.

This form of penetration hardness actually measures resistance to plastic flow. Crystal chipping, crystal position, amount of load, rate of load application and operator interpretation are factors governing the accuracy of the measurement (see Table 1).

Toughness as a property is defined as the ability of an abrasive to withstand the forces brought to bear upon it when in use. Specific applications often require a greater or lesser degree of toughness in an abrasive material so that an abrading operation may be performed properly. The toughness of abrasives may be varied chemically; for example, pure aluminum oxide is relatively brittle, but by the addition of up to 3% titania its toughness can be substantially increased.

The measurement of toughness is generally performed by ball milling or by shooting of the abrasive grains against a barrier. In either case, the degree to which the particles are broken down or reduced in size is inversely proportional to their toughness. Grinding tests have correlated well with toughness tests performed in this manner.

Chemical Activity (21,22). Because considerable heat is sometimes generated during abrasion, any chemical activity existing between the abrasive and the abraded article will be greatly accelerated at the point of abrasion. Generally the best abrasive for a given operation is the one which is most nearly inert with respect to the material to be ground, although in most loose-abrasive applications the heat generated is insufficient for chemical activity to become a factor.

The classic examples of the effect this property can have upon the performance of an abrasive are the poor efficiencies obtained when glass is ground with aluminum oxide and when steel is ground with silicon carbide. Aluminum oxide is soluble in glass, and silicon carbide is soluble in steel. At the elevated temperatures at which grinding takes place, these solubilities are increased and their effect on abrasiveness is pronounced. Solubility is also the reason why such hard compounds as titanium carbide and vanadium carbide are unsatisfactory as abrasives, and the difficulties encountered in grinding titanium can be traced to the extreme solvent action this metal has on all known abrasives.

Heat Conductivity. Heat conductivity is an important factor primarily in the selection of abrasives for use in bonded products. Zirconium oxide has a Knoop hardness of only 1160 (compared to 2460 for silicon carbide) yet it has been shown to be an extremely efficient abrasive on certain materials. This efficiency has been at-

Table 2. Abrasive Materials

Natural abrasives			
<i>Superior hardness (above 7 in Mohs' scale)</i>			
diamond	corundum	emery	garnet
<i>Intermediate hardness (5.5 to 7 in Mohs' scale)</i>			
Silica abrasives			
buhrstone	chert	quartz	sandstone
chalcedony	flint	quartzite	silica sand
Other rocks and minerals			
argillaceous limestone	feldspar	perlite	quartz conglomerate
basalt	granite	pumice and pumicite	
	mica schist		
<i>Inferior hardness (below 5.5 in Mohs' scale)</i>			
apatite	diatomite	rottenstone	talc
calcite	dolomite	siliceous shale	tripoli
chalk	iron oxides	silt	whiting
clay	limestone		
Manufactured abrasives ^a			
boron carbide	fused alumina	periclase (artif)	
calcium carbonate (pptd)	glass	silicon carbide	
calcium phosphate	iron oxides	tantalum carbide	
cerium oxide	lampblack	tin oxide	
chromium oxide, Cr ₂ O ₃	lime	titanium carbide	
clay (hard-burned)	magnesia (pptd)	tungsten carbide	
diamond	manganese dioxide	zirconium oxide	
		zirconium silicate	

^a Also included are metallic abrasives, such as steel wool, steel or iron shot, angular grit, brass wool, and copper wool.

tributed, at least in part, to the low heat conductivity of this abrasive. Because zirconium oxide does not heat readily, it does not expand and crack or heat and char the surrounding socket of bond, and thus it can strike the surface of the object being ground many more times before being sloughed off (see Abrading process, page 42).

Abrasive Materials

Abrasive compounds (2,4-7) can be broadly classified as natural and manufactured. Ladoo (4) gives a comprehensive classification shown in Table 2.

NATURAL ABRASIVES

Only a few natural abrasives (3-5,8) have gained industrial significance. Most have been gradually replaced by their more uniform and generally more efficient manufactured counterparts. Some of the more important natural abrasives still in substantial production are the following:

Diamond (see Carbon). With a Knoop hardness rating of 8200 to 8500, diamond (natural or manufactured) is one of the two hardest substances known. (The other is cubic boron nitride.) Although all diamonds are carbon in a crystalline form, industrial diamonds occur as three types. *Bort* is diamond in single crystal fragments which are off-color or otherwise unsatisfactory for gems. *Ballas* consists of spherical masses of minute, intergrown diamond crystals arranged more or less concentrically. *Carbonado* is a mixture of diamond, graphite, and amorphous carbon; it is the toughest form of industrial diamond. The latter two types are found mainly in Brazil, but *bort*, found mostly in Africa, makes up more than 90% of all industrial diamond production.

World production of industrial diamonds in 1959 was 20,900,000 carats (one carat = 0.2 g) and was valued at 78.7 million dollars.

Abrasives applications for industrial diamonds include their use in rock drilling, as a tool for the truing of grinding wheels, in polishing and cutting operations (as a loose powder), and as the material providing the abrasive action in grinding wheels.

Corundum (see Aluminum compounds) is a naturally occurring massive crystalline form of aluminum oxide and is an impure form of ruby and sapphire gems. Formerly corundum was used extensively in grinding wheels but today it is mainly employed as a loose abrasive to grind and polish optical lenses. Some manufacturers maintain that it is better for this purpose than artificial aluminum oxide. World production in 1959 of this once important abrasive was only 8000 short tons, all of which came from Africa.

Emery is an intimate mixture of corundum (Al_2O_3) and magnetite (Fe_3O_4), with or without hematite (Fe_2O_3), and varying in hardness and toughness according to the iron oxide present. Sources of the best grades of this material are Greece, Turkey, and the United States. Emery is generally reddish-black in color but may vary from dark gray to blue black, depending on the place of origin.

At one time most manufactured grinding wheels were made with emery as the abrasive, but today the chief application of emery is in the construction of nonskid concrete floors and pavements. A total of 8500 short tons of emery was sold or used in the United States in 1959.

Garnet is the name given to a group of minerals possessing similar physical properties and crystal forms but dissimilar chemical compositions. Seven species

exist, all of which are silicates. Their general formula is $3\text{RO} \cdot \text{R}_2\text{O}_3 \cdot 3\text{SiO}_2$, the divalent element being calcium, magnesium, iron, or manganese, and the trivalent element aluminum, iron, chromium, or titanium.

Color varies greatly and includes white, pale green, pale yellow, deep green, deep red, and black. Garnet ranges from 6 to 8 on Mohs' scale. The majority of the world's garnet production comes from the Adirondack Mountains in New York State although Idaho in the United States and Morocco, Madagascar, and Tanganyika produce small quantities. Industrial use is primarily confined to paper and cloth products (45%), the grinding of optical lenses (35%), and sand blasting (20%). U.S. production in 1959 was 14,500 short tons valued at \$1,211,000.

Quartz, Quartzite, Silica Sand, and Sandstone. Quartz is crystalline SiO_2 (see Silica). Sandstone is grains of quartz bonded or cemented by another compound, such as iron oxide, clay, calcite, or quartz. In the latter case, if the bonding is very firm, the rock is known as quartzite.

Quartz is used in the abrasive industry on "flint" sandpapers. It is cheaper than garnet and has maintained a small market on this basis. It is also used as an abrasive in hand soaps, scouring compounds, metal polishes, etc. In 1959, the U.S. consumption of quartz and quartzite for abrasive purposes was 65,000 short tons valued at \$320,000. Use of these materials for all purposes in the same period was 17,080,000 short tons.

The abrasive uses of silica sand include sand blasting, glass polishing, sawing stone (as cutting sand), and burnishing gold decorations onto porcelain. Sandstone, once quarried and shaped into grinding wheels, is now quarried only for the building trade. In the United States, 2,044,000 short tons of sand and gravel was used for abrasive purposes in 1959, at a total value of \$7,259,000.

Pumice and Pumicite. Pumice is a highly cellular, glassy, volcanic lava. Pumicite has the same characteristics and origin, but was blown into small particles during formation. Germany, Italy, and the United States, in that order, lead the world production of these materials. Although world production of pumice and pumicite has risen steadily since 1950, abrasive uses have sharply declined. Only 12,000 short tons was used as abrasive in the United States in 1959 compared to 63,700 tons in 1945. Total world production in 1959 was 10,300,000 short tons.

Major abrasive uses of pumice and pumicite are for dressing the wood and metal surfaces of furniture and musical instruments during manufacture, for preparing metal surfaces prior to silver plating, as a stone cleaner in lithography, for rubbing and polishing fine tools, for scouring in restaurants, and as ingredients of domestic cleaning and scouring preparations.

Tripoli (not to be confused with tripolite, a diatomaceous earth found in Tripoli, North Africa) is the general name for a number of fine-grained, lightweight, friable porous forms of decomposed siliceous rock, found in Missouri, Oklahoma, Arkansas, and Georgia. Rottenstone and microcrystalline silica are similar to tripoli. These materials are used in buffing compounds, on buffing wheels, in scouring soaps and powders, and in polishes; a very finely sized white grade known as "white rouge" is used for polishing optical lenses. Tripoli (including rottenstone and microcrystalline silica) used for abrasive purposes in the United States in 1959 was 34,398 short tons.

Miscellaneous Natural Abrasives. Ground feldspar appears in many scouring and cleaning compounds and as a window cleaner. China clay (kaolin) is sometimes used in polishing powders, and calcined clay is also used for lens polishing.

MANUFACTURED ABRASIVES (2,4-6,8,9)

As automation continues to push the human being ever further from the point at which operations take place, the factor of reproducibility takes on ever greater significance. When abrading operations were performed by hand or on hand-operated machines, the batch-to-batch variations in natural abrasives were of little consequence because they could be compensated for by the operator. Modern designing and engineering demand that machine tools perform in an identical manner from tool to tool to allow machining cycles to be programmed and fitted into long, automatic production lines.

The reproducibility of manufactured abrasives made it almost inevitable that they would eventually dominate the abrasives market as they do today. In 1959 the United States and Canada produced 191,000 short tons of aluminum oxide and silicon carbide (most of it for abrasive purposes) compared with a natural-abrasive production of about 79,000 short tons (exclusive of sand and gravel). New artificial abrasives and refinements of existing materials have added to the versatility of the abrading process. The following descriptions cover manufactured abrasives:

Silicon Carbide (SiC) (see Carbides). Two types are produced, a gray or "black" and a green. The latter is somewhat purer than the former and probably slightly harder, although there is some question about this. Silicon carbide is used to grind cast iron, nonferrous metals, and nonmetals. World production in 1957 of silicon carbide for all purposes was over 150,000 short tons.

Aluminum oxide (see Aluminum compounds) is produced from bauxite in one of three ways.

In the first method, a charge of finely divided low-silica bauxite, coke, and iron borings is placed into a water-cooled furnace shell. Carbon electrodes are lowered into the open furnace and an electrical current is passed until the charge fuses. The iron and coke reduce impurities, which then sink to the bottom of the furnace. The mass is cooled (for about one week), removed from the furnace shell, and crushed. The majority of fused aluminum oxide is made in this manner.

A second method involves reducing bauxite as above, but with the addition of iron sulfide or other sulfides to the fusion. The fusion product is a mass of irregular single crystals of aluminum oxide in a water-soluble glassy matrix. The mass is readily disintegrated and then separated into various sizes.

To produce white fused alumina, the bauxite is first treated by the Bayer process (dissolving the bauxite in caustic soda and then reprecipitating it) to remove almost all impurities. The bauxite is then fused in an electric furnace without further reduction. Just before the mass is cooled about one-half percent sodium oxide is added and its violent reaction produces bubbles in the mass. The result is an abrasive perforated with many fine tubules. It fractures easily and has found extensive use in vitrified grinding wheels.

The toughness of aluminum oxide can be increased by increasing the content of titanium oxide (TiO_2), and several grades varying in color from white to pink to dull gray are being produced. If the molten aluminum oxide is cooled rapidly a small crystal product is obtained, which exhibits extreme toughness and wear resistance in grinding wheels. An even tougher and more wear-resistant abrasive is obtained when finely ground bauxite is sintered in the form of small pellets of a size suitable for abrasive grit.

Aluminum oxide is an almost universal abrasive which will successfully grind most metals and many nonmetals. In 1957, world production of aluminum oxide for all purposes was more than 326,000 short tons.

Diamond (6). (See Carbon.) In February 1955 the General Electric Company announced that their laboratories had successfully produced artificial diamond. They succeeded in this endeavor by subjecting graphite to pressures ranging from 800,000 to 1,800,000 pounds per square inch at temperatures ranging from 2200°F to 4400°F. The use of a molten metal catalyst of either chromium, manganese, iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, ridium, or platinum was the breakthrough which allowed this great accomplishment to take place.

Man-made diamonds 80-mesh and finer are manufactured on a regular production basis and are competing in price and efficiency with the natural stones. Their small size keeps the man-made product in the range of industrial applications even though gem-quality color has been achieved.

It has been reported that man-made diamonds excel their natural counterparts in some operations but this is much disputed. There is no question, however, of their having achieved equality in all industrial applications.

Tungsten carbide (see Carbides), while almost exclusively used as a single-point cutting tool, has found some use as an abrasive. Grits of cemented tungsten carbide are fixed to a metal body and covered with a thin metallic coating. They have shown usefulness in grinding rubber, plastic, and other soft nonmetals.

Boron Nitride. (See Boron compounds.) In 1957 General Electric Company produced a cubic boron nitride and named it Borazon. It is generally black, brown, or dark red, and is as hard as diamond (since it scratches diamond almost exactly as diamond scratches it). Borazon has a heat stability advantage over diamond in that it is unaffected at temperatures at which diamonds oxidize rapidly. The compound is not yet in commercial production.

Metallic abrasives (6) include crushed shot, steel or iron shot, and angular grit. *Crushed-steel shot* is made from high carbon and crucible steel specially treated to impart brittleness. It is then crushed, screened, and heat-treated and is available in sizes of 20–200 mesh. *Steel or iron shot* is chilled cast steel or chilled cast iron separated into small spherical globules by directing high-pressure steam or compressed air against the molten metal. The globules are blown into water, where they are cooled. The shot is then heat-treated and graded into sizes from 7–100 mesh. *Angular grit* is coarse shot which has been granulated and heat-treated. Metallic abrasives sold in the United States in 1959 amounted to 151,700 short tons.

Miscellaneous Manufactured Abrasives. *Steel wool* is made from a variety of steels by shaving or scraping a continuously moving wire with a fixed serrated cutting tool. It is used for finishing wood and soft metals and for scouring and cleaning. *Brass* and *copper wool* are used primarily for domestic cleaning. Many metal oxides and other compounds are precipitated chemically in a very fine grain size and are used as polishing agents. Iron oxide, as *rouge*, is used for polishing glass and a variety of other materials. As *crocus*, a purplish red powder, iron oxide is employed in finishing cutlery and brass. Finally, as *black rouge*, a black magnetic iron oxide, it has some use as an abrasive. *Chromium oxide* is used to polish platinum and stainless steel; *tin oxide*, to polish precious stones. *Cerium oxide* and *zirconium oxide* are also employed in glass polishing. *Manganese dioxide*, *magnesia*, and *calcium carbonate* all

serve as mild abrasives. *Calcium hydroxide* (hydrated lime) is used in buffing compounds for brass, copper, bronze, pearl, and celluloid.

Coated Abrasives

Coated abrasives (10,11) consist of a flexible backing upon which films of adhesive hold and support a coating of abrasive grains. The backing may be paper, cloth, vulcanized fiber (a specially treated cotton rag base paper), or a combination of these materials. The abrasives most generally used are aluminum oxide, silicon carbide, garnet, flint, emery, and crocus.

Once confined to the woodworking shop, "sandpaper" has grown into a versatile, useful, and efficient industrial tool. A myriad of machines ranging from portable grinders to giant surface grinders and roll grinders now utilize coated abrasive products. *Abrasive-belt machines* perform centerless, swing-frame, and floorstand operations once reserved for grinding wheels.

Wearable *coated-abrasive wheels* of the radial-flap type (see Fig. 5, p. 40) can grind and polish contours that are almost impossible for bonded abrasives to accomplish. Coated-abrasive *bands*, *sleeves*, and *cartridge rolls* (coated abrasive wound around a spindle into a multilayered straight or tapered cartridge) have added to the utility of this product. Coated-abrasive *discs* are widely used on a variety of disc grinders.

In manufacture, the first step is the "making process." Here a smooth film of either hide glue, phenolic resin, synthetic varnish, or a combination of a mineral filler and one of the preceding is laid upon the backing. (Hide glue is used as the adhesive in about 55% of all coated products. It has a high initial strength but will soften in water and get gummy in high humidity. Phenolic resin is used when very rugged operations are to be encountered and where waterproofing is necessary. About 35% of the coated products are made with this coating. The others are made with a varnish coat and are limited to paper production for wet applications.) The thickness of this "make coat" is dependent upon the grit size of the abrasive to be applied.

The abrasive is next deposited onto the coated backing, either mechanically or electrostatically. (In the latter process each grain is drawn electrically to the backing surface in such a manner that the flat sides of each grain are made to adhere to that surface, and the abrasive points to face outward from it. This method is particularly useful in the manufacture of coarse grit paper or cloth products because it gives a freer, faster cutting product.) Grit sizes range from 12 to 600, and the particles may be "close" (closely packed together) or "open" (sparse). Close coating is most often employed; sparse coating is used when soft gummy surfaces are to be abraded because it is essentially nonclogging. Open coatings cover from 50 to 70 percent of the coated surface with abrasive.

After drying, the "size coat," usually of the same material as the "make coat," is applied. It adheres to the "make coat" and reinforces the abrasive. A final drying completes the operation, after which the finished product is wound into large rolls and stored for later conversion. Many resin-bonded products require additional curing at elevated temperatures in roll form. When loading or clogging of the abrasive grits by the material being ground is a problem, as in the finishing of furniture, a coating of zinc stearate is sometimes applied over the size coat.

In order to transform the large rolls into consumer products, certain finishing or converting operations are necessary. The first of these is usually *flexing*. This is

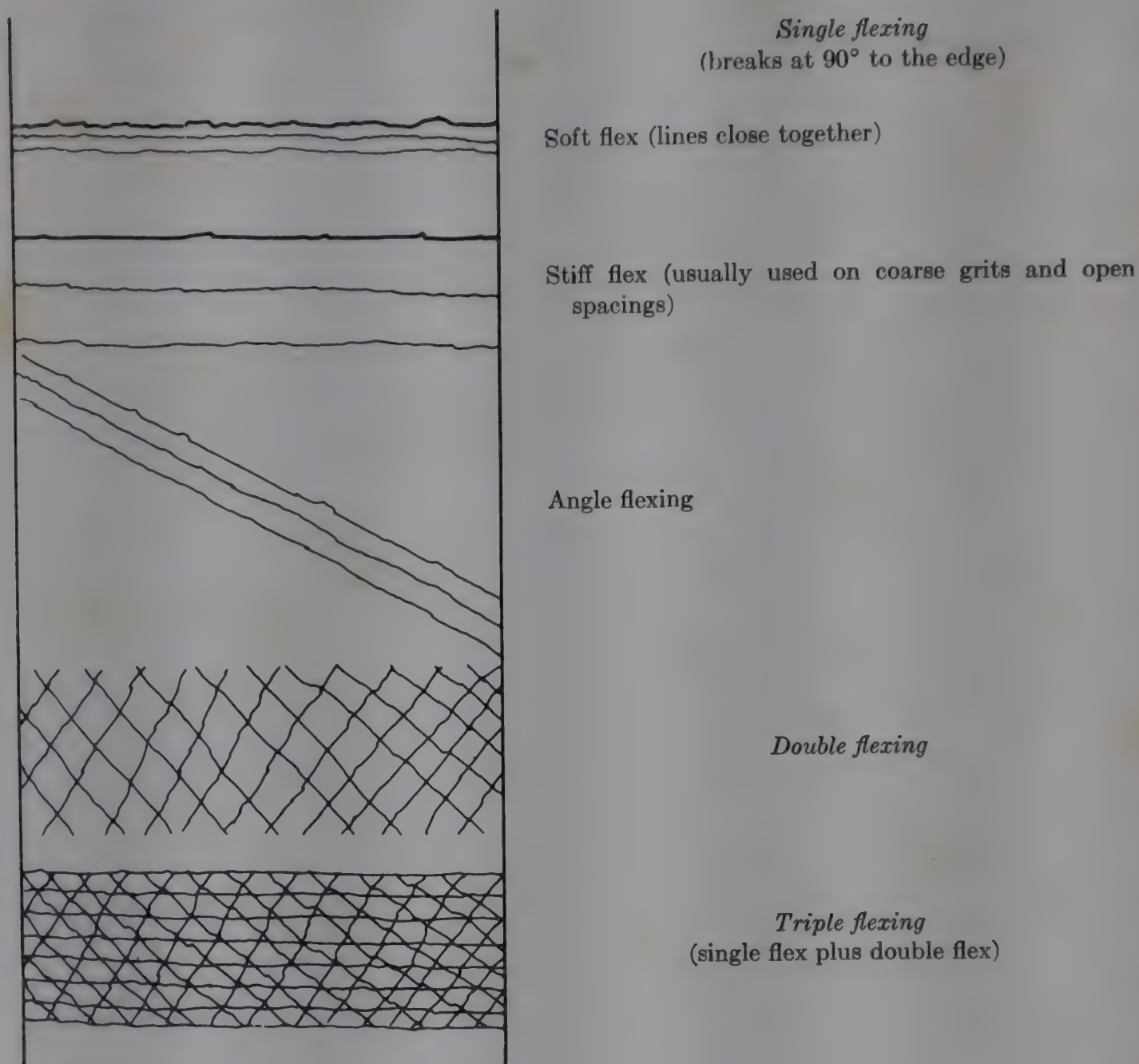


Fig. 1. Flexing operations (10).

the controlled cracking of the adhesive layer in such a way that the discontinuity of this layer will allow the product to flex or bend. Some items (garnet or silicon carbide finishing paper, for example) do not require flexing, but the majority of paper and cloth products are *single-flexed*, ie, passed over a bar at an angle of 90°. “Soft flex” and “stiff flex” as shown in Figure 1 are achieved by varying the diameter of the bar over which the paper or cloth is passed. *Double flexing* is accomplished by flexing the sheet at two 45° angles to its lengthwise direction. Certain glue- or resin-bonded aluminum oxide cloth products ranging from 80 to 320 grit are treated in this manner. *Triple flexing* is a combination of single and double flexing and is employed when the product must grind very sharp or irregular contours (see Fig. 1).

Coated abrasives are supplied in widths ranging from 1/4 to 50 inches in standard 50-yard rolls. They are also formed into sheets, discs, and molded coils or rolls. Belts are regularly supplied 1/4- to 88-inches wide and have been made up to 120-inches wide.

The following operating data with regard to finish and operating speed of abrasive belts are of interest:

Finish. The harder the bond the coarser will be the finish, thus a resin-bond finish is coarser than a glue-bond finish.

High belt speeds generally give a better finish as well as less glazing and loading, and faster stock removal.

A harder contact wheel gives a coarser finish; a high-durometer rubber wheel, while fast-cutting, will therefore give a coarser finish than a soft-rubber or canvas contact wheel.

The use of coolants and lubricants produces a finer finish.

Belt Speeds. The optimum belt speed in terms of such factors as belt life, production, and finish is usually governed by the material being ground (see Table 3).

Table 3. Optimum Belt Speeds

Materials to be ground	Surface, feet per minute	Conditions
mild steel	4000–5500	heavy grinding
	5000–7000	polishing
nonferrous metals (aluminum, zinc, copper)	5500–7500	heavy grinding (with lubricant)
	6500–8500	polishing with lubricant
plastics	4000–5000	wet
thermoplastic or thermosetting resins	2000	grease-stick lubricant applied to belt during operation (see Grinding fluids, page 38)
	800–100	dry

The rise in the sale of coated abrasives in the United States has been steady. Only about 12 million dollars in 1938, sales amounted to 117 million dollars in 1959. As with any tool, this increase resulted primarily from the introduction of new machines and the wider application of existing designs. The versatility of the abrasive belt, now used for honing, precision grinding, polishing, and snagging, was responsible for much of the increase.

Bonded Abrasives

Bonded-abrasive products (12–15) are abrasive grains bonded into three-dimensional objects. These include grinding wheels and segments, honing sticks, dresser sticks, and sharpening sticks. Of these, the grinding wheel is the most important in terms of production volume and versatility of application.

A grinding wheel (or other bonded-abrasive product) is composed of abrasive grains, a bond or matrix in which the grains are held, and pores or void spaces. The following factors govern the suitability of a wheel for a particular application: (1) abrasive type, (2) grain size, (3) grade, (4) structure, (5) bond type.

Grinding wheels are identified by a standard marking system which designates these variables to the consumer and aids him in recognizing wheels designed for specific purposes. Symbols for each factor vary among manufacturers, but by position in the marking they refer to the same aspect of the wheel.

TYPE OF ABRASIVE

The choice of abrasive for a grinding wheel lies between aluminum oxide, silicon carbide, and diamond. The major use of aluminum oxide is in grinding steel. Soft

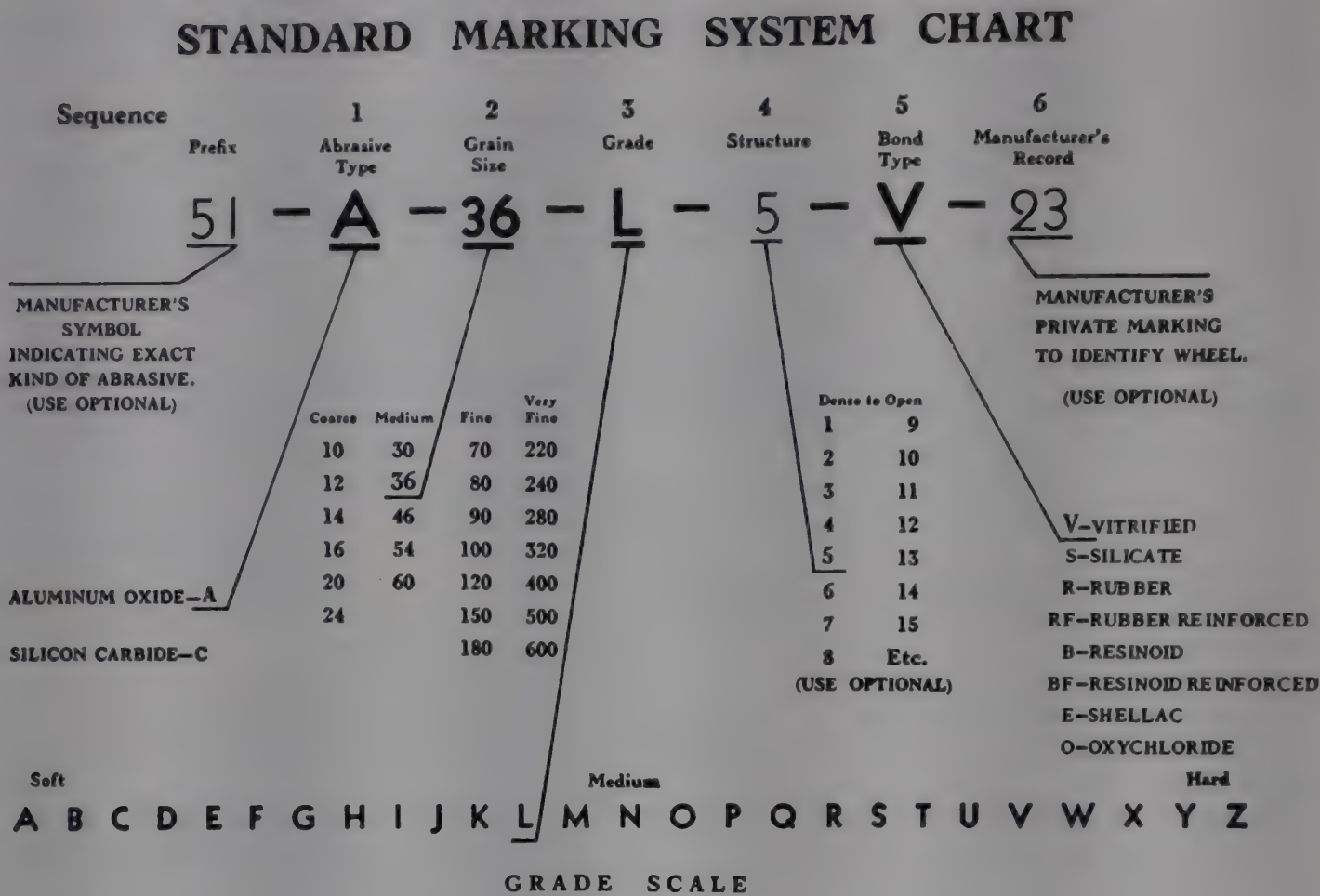


Fig. 2. Standard wheel markings (16).

steels are ground with a tough, titania-containing aluminum oxide; the harder, wear-resistant steels require a purer, more friable (easily fractured) abrasive; and for extremely heat-sensitive, wear-resistant steels a white, pure, and very friable aluminum oxide is specified.

Silicon carbide finds application in the grinding of cast iron, nonferrous metals, and nonmetals. The purer green silicon carbide grinds cemented tungsten carbide where light removal is involved. Diamond is used for tungsten carbide grinding and cutting off and will be discussed in a separate section.

GRAIN SIZE

The degree of roughness of the surface generated by a grinding wheel is mainly dependent upon the size of the grains (23) in the wheel. Available grain sizes (also referred to as grit sizes) according to the U.S. Department of Commerce Grain Standards (U.S. Standard Sieve Series) are as follows:

Silicon carbide and aluminum oxide

Classified grain sizes

8, 10, 12, 14, 16, 20, 24, 30, 36, 46, 54, 60, 70, 80, 90, 100, 120, 150, 180, 220, 240

Unclassified flours

F, 2F, 3F, 4F, and XF

Classified flours

280, 320, 400, 500, 600

Table 4 will be helpful in aiding the reader to visualize the size of the grains referred to throughout this article.

Table 4. Grain (or Grit) Sizes

Abrasive grain no.	Control sieve opening, inches	Abrasive grain no.	Control sieve opening, inches
10	.094	60	.011
12	.079	70	.010
14	.066	80	.008
16	.055	90	.007
20	.047	100	.006
24	.033	120	.005
30	.028	150	.004
36	.023	180	.0035
46	.016	220	.0029
54	.014	240	.0029

Abrasive-grain size numbers represent standard mixtures of grits screened by U.S. Standard Sieves. These numbers were developed by abrasive-grain manufacturers in conjunction with the U.S. Department of Commerce and the National Bureau of Standards and represent a practical solution to the problem of representing the size of abrasive grains.

The following surface qualities obtained with a ceramic-bonded wheel in a cylindrical operation are indicative of the effect of grain size (11):

Grain size	Surface finish (average microinch roughness)
46	rougher than 32
54	20-32
60	15-20
80	10-15

BONDS

In the manufacture of most bonded abrasive products either a ceramic bond or a resinoid (phenolic resin) bond is used. Rubber, sodium silicate, magnesium oxy-chloride, metal, and shellac all are employed to bond abrasive grains and have utility for specific applications.

Ceramic (Vitrified). About 45% of the grinding wheels manufactured are bonded with a glass or porcelain. Wheels made with aluminum oxide abrasive are bonded with glass and, at the firing temperature (about 2300°F), as the glass is formed, it dissolves a very thin layer of the abrasive. Silicon carbide is sufficiently active to decompose in the presence of a glass at elevated temperatures and is therefore frequently bonded in a reducing atmosphere with a porcelain less reactive than glass.

Ceramic-bonded wheels are used for precision work in cylindrical, internal, surface, centerless, and tool-room applications. They are also utilized to some extent in high-removal, heavy-duty grinding but, because ceramic-bonded wheels are subject to thermal shock, resin-bonded products (which are tougher, resilient, and can be safely operated at higher speed) have replaced them in most of these operations.

The color of ceramic-bonded products is most often imparted by the abrasive because the bonding agent is generally colorless. Thus, if white aluminum oxide is

used the resulting wheel is white, with green silicon carbide a green wheel is produced, and a tougher aluminum oxide imparts its blue fired color to the wheel.

Resin. About 40% of the grinding wheels produced are bonded with a phenolic resin (see Phenoplasts). Because this resin cures or irreversibly hardens at 300–400°F, no problem with abrasive reactivity exists. Another advantage of this low processing temperature is that it allows the addition of fillers to the bond. When compounds such as potassium fluoroborate (KBF_4), potassium sulfate, and sodium chloride, in combination with iron sulfide (FeS_2), zinc sulfide, and antimony sulfide are included in the grinding wheel bond, they melt at the grinding interface and lubricate the surface of the metal being ground. They also tend to prevent the ridges raised by the abrasive from rewelding into the body of the metal, and thus increase the efficiency with which the wheel performs (13).

Resin-bonded wheels are used where large amounts of metal must be removed in a short time, as in grinding with abrasive discs, in steel-mill snagging and foundry snagging, and in cutting-off operations. They are also used to a limited extent in precision grinding.

Three characteristics prevent large-scale application of this product on precise operations. First, resin-bonded wheels are resilient and the “spring” in the wheel is sufficient to make very exact tolerances unattainable. Second, because the bond is rubbed and/or charred away during grinding (as opposed to being chipped or broken away in ceramic wheels) a higher temperature is imparted to the workpiece by a resin-bonded wheel. The consequent expansion in the workpiece limits the accuracy with which it can be finished. Third, the resin–abrasive interface is attacked by coolant and the longer a resin-bonded wheel exposed to coolant is in use, the softer it acts. By treating the abrasive with a silicone the adverse effect of coolant on resin bonds has been substantially reduced.

Rubber. One of the earliest bonding materials and once the most important organic bond, rubber is now used mainly in the manufacture of thin wheels for slicing or cutting off, and of fine grit wheels for generating very smooth finishes. In manufacture the abrasive grain is mixed with crude rubber, sulfur, and other ingredients for curing, and then is passed through calender rolls to produce a sheet of specified thickness. The wheels are stamped from this sheet and heated under pressure to vulcanize the rubber.

Shellac. Some wheels for finishing steel mill rolls and a few cut-off wheels are made with shellac bond. The abrasive grain and shellac are mixed in steam-heated kettles and rolled or shaped to the desired size. Most shellac wheels have been replaced by the more efficient resin bond.

Silicate. Silicate of soda and abrasive grain form wheels with a very soft grinding action after drying at a moderate temperature. The use of this bond is virtually nil, because it is outperformed by ceramic and resin bonds.

Magnesium Oxychloride. MgO and MgCl_2 mixed with water and abrasive grains will cold-set to form a grinding wheel. This bond has some use in disc operations but is attacked by coolants and grows progressively harder as it ages. These drawbacks have severely limited its use.

GRADE AND STRUCTURE

The percentages by volume occupied by abrasive, and by bond, profoundly affect the properties of the wheel, but since there almost always are open pores in the body

of the wheel, the system is in effect one of three components, and two parameters are required to express its composition. The parameters used are *grade*, which depends on the volume percent of bond, and *structure*, which depends on the percent of abrasive, and refers to the spacing of the abrasive particles.

Grade. The volume percent of bond may vary from 4 to 48%. A smaller percentage of bond gives a "soft" wheel, in which the dulled abrasive particle is easily detached from its socket before the heat produced by friction can damage sensitive materials. "Hard" wheels have sufficient bond to retain a firm hold on an abrasive subjected to heavy grinding pressure, making the rapid removal of metal possible without excessive wheel wear. The *grade* is noted by a letter, and *ranges from A (soft) to Z (hard)*.

Structure. The spacing of the abrasive particles affects grinding rate and rate of removal, and is helpful in making slight variations in wheel performance to suit specific requirements. The volume percent of abrasive may vary from 48 to 60%. When the natural packing characteristic of the abrasive is denser than is required, a more open structure is attained by the addition of a material such as naphthalene or *p*-dichlorobenzene; this type of material sublimes during firing or cure, leaving induced pores and wide grain spacing. The *structure* is indicated by a numeral, and *varies from 1 (closed) to 15 (open)*.

Because the amounts of abrasive, bond, and voids within a wheel are interrelated in a three-component system, a change in one of the components must affect at least one other factor. If abrasive is held constant (and thus structure number is constant) a change in bond will inversely affect the voids (by increasing or decreasing the grade). Similarly, if bond is held constant a decrease in structure number (increase in abrasive content of the wheel) will reduce the void content of the wheel.

METHOD OF MANUFACTURE

Resin- and ceramic-bonded grinding wheels are manufactured by first mixing the abrasive and bond together. The abrasive is wet with a liquid in which a portion of the bond is soluble (water for ceramic bonds, liquid phenolic resin or furfuraldehyde for resin bonds) and the bond is coated to the abrasive grits in a mixing machine. A weighed portion of the mix is then poured into a mold of the desired size and shape, and the wheel is pressed to a predetermined density. Pressures up to four tons per square inch are employed in this operation.

Charging of the mold with a calculated amount of mix produces a pressed wheel that will contain a known volume of abrasive and bond. It will also contain a known and desired volume of voids.

When the wheel has been formed it is subjected to heat of varying intensity (depending upon the bond) to form the bond into a hard, unreactive mass. Ceramic wheels are fired at about 2300°F, phenolic resin is reacted at 300–400°F.

All ceramic-bonded wheels are pressed cold (the old "puddling" method of wheel forming is no longer used); some resin-bonded wheels, in order to reduce the void content to near zero, are heated while being pressed to liquefy the resin. While the wheel is in this state, air is easily eliminated before the resin hardens, and a dense, pressure-resistant wheel capable of removing up to 700 pounds of metal per hour is obtained.

Finishing operations follow firing or curing. The sides of the wheel are made flat and parallel, hole and circumference are brought in concentricity, special shapes are formed into the face or sides, and the wheel is balanced and tested at a speed above that

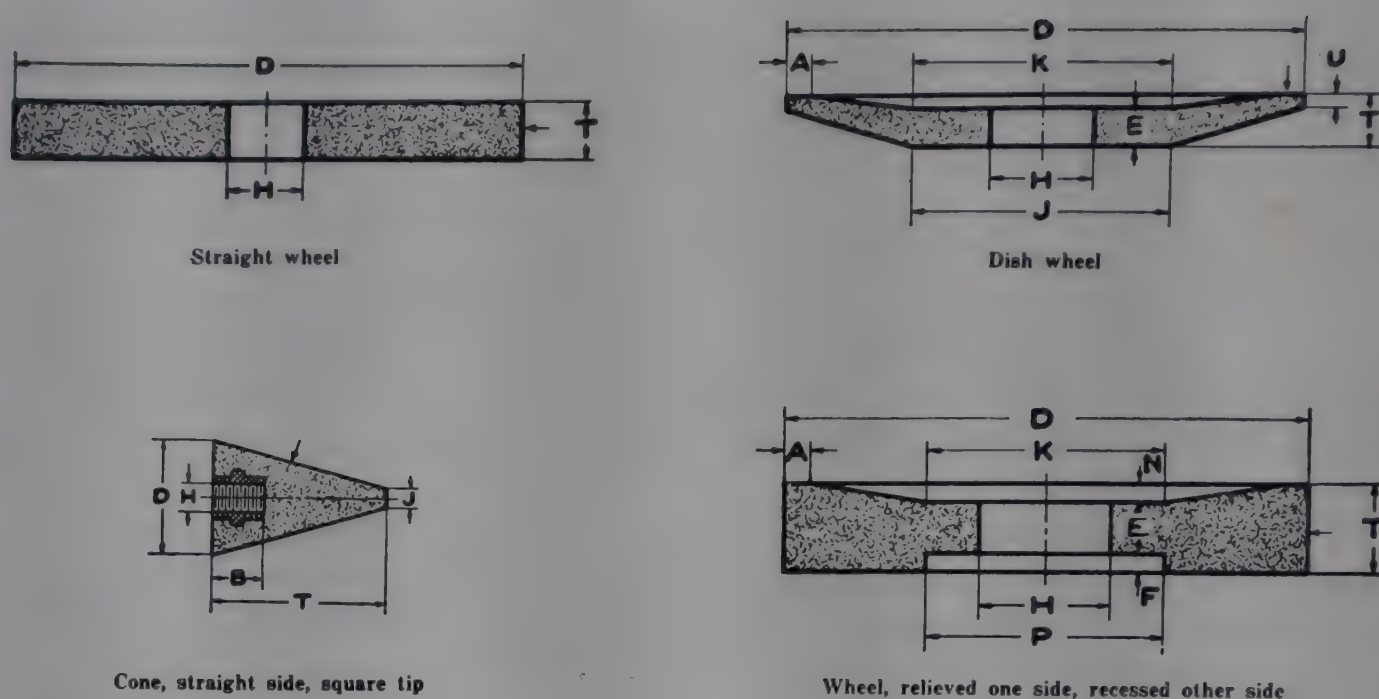


Fig. 3. Shape types of grinding wheels (12). Courtesy Grinding Wheel Institute.

at which it is intended to operate. (See ASA B7.1-1956 *American Standard Safety Code for the Use, Care and Protection of Abrasive Wheels*.)

By pressing resin or ceramic wheels in molds of various shapes, or by shaping ceramic wheels after pressing but before firing, an unlimited variety of forms can be produced. These shapes have been standardized into 27 accepted types having many variations according to size. (See Fig. 3; see also ASA B74.2-1960 *American Standard Specifications for Standard Shapes and Sizes of Grinding Wheels*.)

The wide range of application of the grinding wheel as a metal-removal tool is due to the versatility imparted by this variety of shapes and to the variety of grinding grades in which they can be produced. These two properties represent distinct advantages over single-point cutting tools and coated abrasives.

Net sales of bonded abrasives in the United States in 1959 were slightly more than \$205,600,000.

SPECIAL FORMS OF BONDED ABRASIVES

Honing. Honing is abrasive cutting which involves both rotational and reciprocating motion. Because the resulting grinding pattern is cross-hatched, it makes an ideal oil-retaining surface for bearings and engine cylinders.

Internal honing is performed by bonding abrasive "sticks" inserted into a tool. The tool is cylindrical and somewhat smaller than the bore to be ground. The sticks can expand away from the tool and grind irregularities in the cylinder. Honing is capable of correcting out-of-round, taper, bell-mouth, bowing, or barrel-shaped bores. *External honing* can be done by either sticks or "tapes." The latter are coated abrasives and have particular application in the bearing industry.

Honing is performed with a coolant. The composition varies but it usually contains 60–90% kerosene and a remainder of cutting oil.

Hones are available in grit sizes 36–600, but 80–400 is the range of practical application. Silicon carbide, aluminum oxide, and diamond are supplied in ceramic, resin, and metal bonds. The greatest number of hones are ceramic-bonded Al_2O_3 or SiC. Bonded hones are identified by a similar system as are grinding wheels.

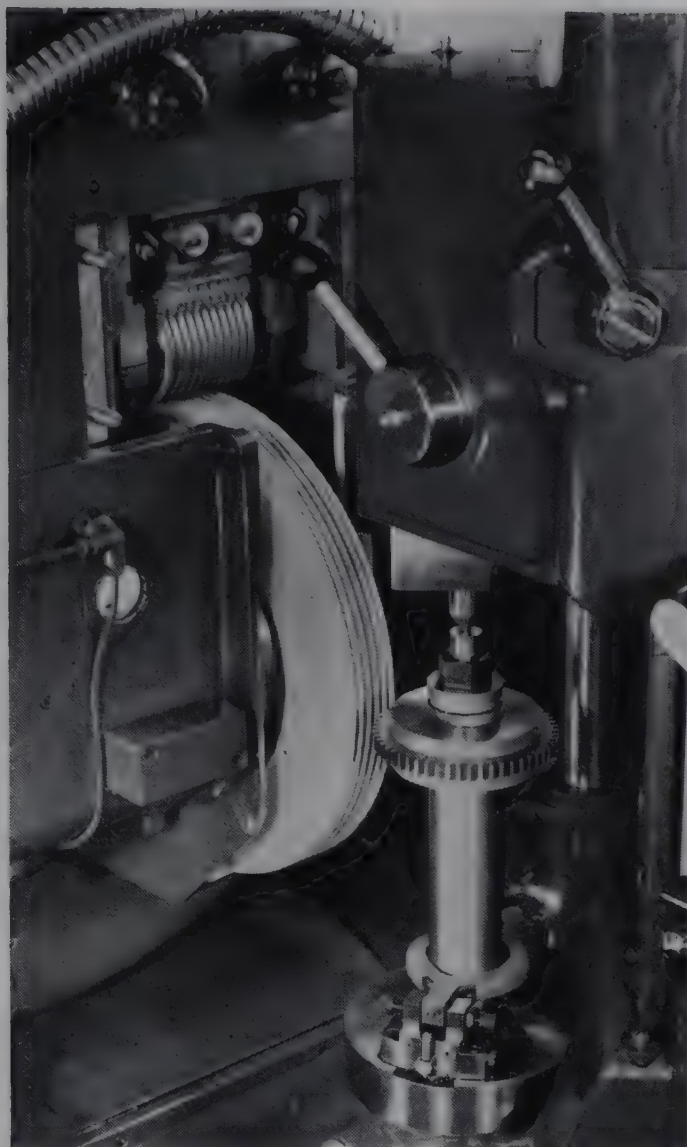


Fig. 4. Crush-form grinding (safety guard removed for clarity). Courtesy The Sheffield Corporation. The free-spinning crusher roll, above, produces in the wheel a shape which is then reproduced in the workpiece (foreground).

Superfinishing is a means of improving the outside surfaces of a cylinder. It performs the same function that honing performs for internal and lapping for flat surfaces. In superfinishing, an abrasive block is applied with pressure to a rotating workpiece. As the workpiece rotates, the stick or block is reciprocated and a finish of from 1 to 60 microinches, depending upon conditions, is generated.

Vitrified bonded aluminum oxide and silicon carbide stones are employed in this process, usually with a lubricant. The process was originally developed for use on automotive bearings, but is now widely applied to a variety of materials and parts in many industries.

Diamond wheels are manufactured with resin, ceramic, or metal bonds. They differ from other bonded wheels in that the diamond section is only a fraction of an inch thick. Resin- and ceramic-bonded diamond wheels are processed in a similar manner as their aluminum oxide and silicon carbide counterparts but metal-bonded wheels are made by means of powder-metallurgy techniques. Centers for metal-bonded wheels may be plastic, steel, or bronze. The bond which holds the diamonds is usually bronze or a bronze alloy although many metallic combinations have been and are being utilized for this purpose.

Diamond wheels are available from 16 to 2000 grit, but 46 to 400 is the range used in most applications. The diamond wheel was originally developed to grind cemented-

tungsten carbide cutting tools, but it has also found wide use in the glass industry and in cutting-off wheels employed on concrete, marble, and stone.

Truing wheels and dresser sticks are vitrified, bonded silicon carbide bodies for conditioning the face of a grinding wheel. *Truing wheels* are ball-bearing-mounted in a holder that is rigidly secured to the grinding machine. Their purpose is to bring the wheel into concentricity and to recondition the face if it is loaded or glazed. *Dresser sticks* are hand-held tools designed to rough the face of a glazed wheel in order to expose sharp, free-cutting abrasive edges.

Crush-form grinding is a means of generating intricate patterns in the face of a grinding wheel; the opposite contour is then developed in the workpiece. Before this method of shaping the face of the wheel was developed, single-point diamonds provided the only satisfactory means of shaped-face generation in grinding wheels, and the intricacy of the face that could be generated was severely limited.

In crush-form grinding a free-spinning roll of hardened tool steel or cemented tungsten carbide having the contour desired in the workpiece is forced into the face of a spinning vitrified wheel. The crusher roll (see Fig. 4) generates a pattern on the face of the grinding wheel by crushing it. When the wheel is plunged into the workpiece (in cylindrical or centerless operations) or downfed as it moves along the piece (in surface grinding), the pattern in the face of the crusher roll is formed in the workpiece. Operations previously turned and then finish-ground can be produced in one grinding operation by this process.

GRINDING FLUIDS

Grinding fluids (17), colloquially "coolants," are fluids employed to cool the workpiece and to act as a lubricant for the abrasive during grinding operations. Heat develops in grinding operations because chips are formed as the abrasive grit passes through the workpiece. The chips are pulled or torn from the main body and friction heat is generated in this process. The majority of this heat is absorbed by the workpiece but smaller amounts are carried away by the chips and by the abrading tool. Many materials are damaged if heated locally to a temperature that is critically high (near 1400°F), and a grinding fluid directed at the point of contact between the tool and the work minimizes this effect by reducing the amount of heat generated and by increasing the rate at which the workpiece returns to an ambient temperature.

Grinding fluids may be classified as grinding oils, soluble oils, chemical fluids, and gases; solids that liquefy at the tool-workpiece interface may also act as grinding fluids.

Grinding oils are mineral oils containing additives such as fatty organic and sulfur-containing organic compounds. They reduce heat generation by providing lubrication, but have a low heat conductivity and are not effective in bringing the workpiece back to its original temperature. Grinding oils work best in operations such as contour grinding, or form grinding, which involve narrow areas of contact between the tool and workpiece.

Soluble oils are water emulsions of petroleum products and represent a compromise between the lubricity of grinding oils and the heat-absorption ability of water. The ratio of water to oil may vary from 10:1 to 100:1. Soluble oils are the most widely used grinding fluids.

Chemical fluids (often referred to as synthetic coolants) are water-base emulsions in which little or no mineral oil is present but which may contain a wide variety of

organic or inorganic compounds. Some of the more commonly used additives are waxes, fatty organic compounds, organic compounds containing sulfur or chlorine, amine soaps, sodium carbonate, and sodium nitrite. Most chemical fluids contain a wetting agent and their main function is lubrication. A few contain chemicals which react with the work surface and thus aid in metal removal, whereby heat generation is reduced.

Air is the most obvious gaseous grinding fluid. The effectiveness of air as a grinding fluid was demonstrated when grinding was performed in an atmosphere of three gases: argon, air, and chlorine. Argon was the least efficient of the three, air was intermediate in efficiency, and chlorine was by far the most efficient. Since the ability of these gases to carry heat (by conduction or convection) is approximately equal, the difference in efficiency has been ascribed to their relative ability to react with the material being ground. The grinding efficiency in a near vacuum was about equal to that in argon (14,17). Carbon dioxide and water mist are other gaseous coolants which have been used.

Wax, sulfur, and rosin are employed to impregnate grinding wheels; these solids lubricate or cool as they melt at the grinding line. Stearates, grease, or similar compounds are applied to coated abrasives. They are usually applied in stick form to the moving belt and they liquefy as do the solids described above.

Loose Abrasives

Loose abrasive (18,19) is used as the cutting or grinding medium in polishing, buffing, lapping, blasting, wire sawing, and barrel finishing.

Polishing. In terms of surface generation, polishing (15) can be considered the intermediate step between grinding and buffing. The lines of demarcation between these operations are not sharply defined, but it is generally accepted that appreciable metal removal is defined as *grinding*, whereas metal removal sufficient to improve the finish without regard to dimensional tolerances is called *polishing*; thus polishing serves to reduce the irregularities in a surface by removing the peaks of material left from grinding or other operations. *Buffing*, on the other hand, merely folds over surface irregularities to form a smooth reflective surface. It changes the surface roughness without significant metal removal.

Polishing operations can be performed by abrasive belts (see Coated abrasives) or by a unique "flap" grinding and polishing wheel made up of many pieces of abrasive cloth fitted radially around an arbor (see Fig. 5). An older system still much in use is the "shop headed" wheel. This is a wheel formed of fabric (canvas, muslin, felt) or leather and coated with an abrasive by the user. The woven materials are usually stitched or glued together to form a wheel, but leather can be wrapped around the periphery of a wooden wheel base.

To coat or "set up" the polishing wheel it is usually heated to 100°F and the face of the wheel is brushed with hide glue heated to about 130°F. The wheel is then rolled in a trough of loose abrasive of the desired grain size and is dried and "cracked," an operation that resembles flexing in coated abrasives. The periphery of the wheel is struck diagonally across the face with a round bar at 45° angles to form "X" cracks in the face. Such wheels, when worn, can be recoated many times before being discarded.

Canvas wheels are used with 24–46 grit for heavy work and where slight imper-

fections must be removed. Muslin is a suitable backing for coarse or fine work and felt is employed with 150-grit or finer to obtain high finishes.

In the order of finish produced, polishing operations are usually described as roughing, dry fining, greasing, and finishing.

A special application of the polishing principle is glass polishing. The polishing material (rouge, Fe_2O_3 , or ceric oxide, CeO_2) is applied to a revolving wheel or buff in a finely powdered form. The buff may be felt, leather, lead metal, copper, or pitch. This process is probably closer to buffing than polishing, since the operation removes very little if any glass but rather causes the surface to flow, producing the desired smoothness.



Fig. 5. Grind-o-flex wheel for grinding and polishing. Courtesy Merit Products, Inc.

Buffing generates a high lustrous and reflective finish and employs 240-grit or finer. It consists of two operations, “cutting down” and “coloring.” The former is to remove minor imperfections and the latter, which derives its name from the fact that it brings out the true color of the material, produces the final luster and the desired surface. Wheels similar to those used in polishing are employed but the abrasive is incorporated in a grease stick or cake compound which is applied to the face of the wheel.

Artificial-alumina and *silicon carbide* buffing compositions are used to obtain a satin finish on aluminum, steel, stainless steel, and brass. *Tripoli* compositions buff brass, copper, aluminum, zinc, precious metals, nickel, and nonmetals. *Lime* ($\text{Ca}(\text{OH})_2$) gives a high luster on nickel, copper, brass, and plastic when applied in the

“coloring” operation. *Rouge* is used to produce a high luster on precious metals and glass; *crocus*, on some brass work and to finish cutlery. *Chrome oxide* buffing compositions “color” stainless steel and chromium.

Lapping is a process to refine the surface finish and geometrical accuracy of flat, cylindrical, and spherical surfaces. Most of these operations employ loose abrasive although some lapping is done by bonded abrasives.

Generally the workpiece has the loose abrasive forced against it by a plate (the lap), the abrasive being present in a liquid vehicle or carrier. The lap is usually softer than the workpiece and the abrasive is forced into the lap, in which position it cuts the workpiece. When gears are lapped they are often run together and the lapping compound is fed between them.

Diamond, silicon carbide, aluminum oxide, boron carbide, and garnet—in sizes ranging from 60 to 1000 grit and in vehicles such as oil, water, grease, kerosene, and alcohol—are employed in these operations. In general, hard abrasives are used to lap hard materials, and soft abrasives to lap soft workpieces. Diamond is used on cemented tungsten carbide and very hard steel; silicon carbide, boron carbide, and aluminum oxide, on a wide range of materials; and garnet, on reduction gears and nonferrous valves.

Blasting is the throwing of abrasive particles at high velocity. It is used in cleaning metal parts, to impart a particular finish, and to cut various materials selectively. There are three types of blasting: wet (or liquid), dry (or air), and airless.

In wet blasting, synthetic or natural abrasive (but never metal abrasive) ranging from 80-mesh to the finest flour is suspended in water and directed under pressure at the part to be cleaned. Generally this prepares the surface for another operation, such as plating or painting, but some deburring is also done by this method.

In dry blasting and airless blasting, compressed air and centrifugal force, respectively, are the means of propelling the abrasive to the workpiece. Grit sizes ranging from 16 to 240 and abrasive materials such as sand, metal shot, and aluminum oxide are employed in these operations.

Deflashing, deburring, and descaling of metal parts and the engraving of designs on granite, marble, and stone are all done by this method. The facades of stone or brick buildings are cleaned by pressure-blasting their dirt-laden exterior surfaces to expose the clean undersurface.

Barrel finishing is the tumbling or vibrating of metal parts in a barrel to remove burrs and flash and to prepare the surface for other operations, such as plating or painting.

For tumbling, the barrel is usually an octagonal, watertight cylinder, 30–60 inches long and ranging in diameter from 24 to 36 inches. It is usually rubber-lined and capable of rotating at variable speeds forward and in reverse.

Vibrating tubs are usually somewhat smaller because the improved efficiency of this method increases the output per unit. The vibration method, though newer than the tumbling system, is rapidly gaining acceptance because of its greater efficiency.

In the barrel along with the objects to be finished are placed a compound, a medium, and water. Compounds are specially formulated for specific metals and conditions, but usually contain coloring, cleaning, and burnishing materials, antifoaming agents, a water softener, and a rust inhibitor, with or without a fine abrasive. Media (colloquially “chips”) may be natural stone, manufactured abrasive, or bonded abra-

sive grains in the form of chips or shapes. The medium is usually processed to give it a blocky rather than a slivery shape. Bonded shapes may be round, triangular, tubular, or any shape found practical by the manufacturer. Other media used for special purposes are soft steel and zinc, hardened steel, hardwood, nylon, sawdust, and abrasive imbedded in rubber.

Tumbling media range in size from $1\frac{1}{2}$ to 2 in. (00-T) to as small as $\frac{1}{32}$ in. (#12-T).

Miscellaneous Loose-Abrasive Uses. In the stone industry *wire sawing* is accomplished by pulling a wire down through a stone slab while an abrasive slurry is pumped through a hose at the point where the wire enters the stone. This method is faster, generates a better surface, and allows the production of thinner slabs than did previously employed methods, such as sawing. In *lithography* loose abrasive is used to produce a surface roughness which promotes better wetting of the plates. *Antislip flooring* is produced by spreading the abrasive on top of a concrete or asphalt floor that is in the process of drying.

The Abrading Process

The art of manufacturing and using abrasive products is rapidly evolving into a science. Complete understanding of the grinding process is necessary before this evolution can be completed. The study of grinding as related to grinding wheels is complicated by the wide range of application of these wheels. Studies have shown that in a soft, porous wheel grinding with light pressure, the grinding mechanism is different than in a medium-grade wheel used at moderate pressure or in a very dense wheel used with high pressure. The type of bond, shape of the abrasive, type of operation, and type of abrasive all contribute to the manner in which the abraded material is removed. These factors make it difficult to generalize about the mechanism of grinding.

In a grinding wheel or coated-abrasive product the cutting action of a single abrasive grit is often compared to that of a single-point cutting tool. It differs in that the abrasive "plows" a furrow as it moves through the workpiece, in addition to pushing a chip ahead of it as does the cutting tool. Because the temperature at the cutting point of the abrasive is near 1200°C these furrows will reweld into the main body of the metal unless chemically prevented by compounds acting at the point of abrasion. The addition, to the resin bond, of fillers which will melt at the grinding wheel-workpiece interface, chemical additives in coolants, chemicals impregnated in bonded and on coated products, and the gas or mist application of compounds have all been successful in retarding this "rewelding." The result is higher abrasive efficiency in the form of greater removal per unit of abrasive.

All abrasives wear as they grind. The effect of this wear on the cutting process and on the abrasive particle is not completely understood throughout the whole range of application. It has been observed that under certain conditions, when the abrasive is worn to the point where the friction drag and impact forces generated as the particle moves through the abraded body are sufficiently great, the abrasive fractures. The wear cycle is then repeated until the particle is small enough to be completely pulled out of the abrasive body.

Because most artificial abrasives are essentially monocrystalline, the fractures are random and large portions of usable abrasive are often lost during each fracture cycle.

A microcrystalline form of aluminum oxide has shown increased efficiency in high-pressure grinding because smaller portions chip off during each wear cycle, resulting in more removal per unit of abrasive. Sintered bauxite is an improvement over microcrystalline alumina for high-pressure applications because, in addition to losing only a small volume of fractured material per wear cycle, it does not readily transmit heat to the bond. Rapid heating of resin bonds causes the bond socket to char and release the abrasive particle prematurely. The abrasive industry has had aluminum oxide, silicon carbide, phenolic resin, and glass for over sixty years. Major improvements in the efficiency and utility of abrading tools have been made by refining and controlling these products, both as raw materials and as finished tools. It seems clear, however, that further major advances cannot be made by the rerefining, redesigning, or better understanding of existing products.

New abrasive materials will probably form the vanguard of future advances in abrasive technology. Abrasive compounds will probably be tailor-made to grind specific materials and to perform various operations. As understanding of the grinding process increases, compounds will be found whose physical and chemical properties are ideally suited to coated abrasives, grinding wheels, blasting, and other applications. Future development of tailor-made abrasives specifically designed for the operation to be performed and for the material to be worked will greatly enhance the efficiency of the abrading process.

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ABSORPTION

In the chemical industries the process of absorption conventionally refers to the washing (scrubbing) or intimate contacting of a mixture of gases with a liquid so that one or more of the constituents of the gas will essentially dissolve completely, or be absorbed, in the liquid. The purpose of such gas scrubbing operations may be any of the following: product recovery, pollutant removal, process reaction, or possibly a combination of these in which the removal of a pollutant, for example, sulfur dioxide, also provides a valued by-product in the form of sulfuric acid. Several typical examples of applied absorption systems are shown in Table 1. The Stretford process (40), which employs a solution of sodium anthraquinonedisulfonate, is one of the latest developed.

The absorption of light hydrocarbons in oil, or of a solvent vapor, such as acetone, in water, are simple cases of so-called *physical absorption*, in which the process forces are the solubility and equilibrium partial-pressure relationships and the resistances are principally diffusion rates. In cases where the dissolving (or absorbed) gas can react with the liquid, known as *absorption with chemical reaction*, the driving forces become more complex.

Table 1. Typical Commercial Gas Absorption Systems

Treated gases	Absorbing liquid	Absorbed gas constituent	Function
coke oven gas	water	ammonia	by-product recovery
coke oven gas	straw oil	benzene and toluene	by-product recovery
refinery gases	alkaline solutions	hydrogen sulfide	pollutant removal
drying gases in acetate fiber manufacture	water	acetone	solvent recovery
products of combustion	water	sulfur dioxide	pollutant removal
	ethanolamines	carbon dioxide	by-product recovery
wet well gas	kerosene	propane and butane	gas separation
reactor gases in manufacture of formaldehyde from methanol	water	formaldehyde	product recovery
ammonia synthesis gas	ammoniacal cuprous chloride	carbon monoxide	contaminant removal
natural and refinery gases	solution of sodium 2,6-(and 2,7-) anthraquinonedisulfonate	hydrogen sulfide	pollutant removal

Gas-liquid absorption processes are usually carried out in vertical countercurrent flow through packed, plate, or spray towers. The conventional packed tower is simply an empty shell filled with commercially available specifically shaped packing materials. The liquid flows down over the packing and thus exposes a large surface to the gas flowing upward through the interstices. In plate towers the liquid flows down in cascade fashion from plate to plate. During its time of travel across each plate, or tray, the liquid is churned into a froth by the upflowing gas stream. This spreads the liquid surface over a great many gas bubbles rising through the tray liquid.

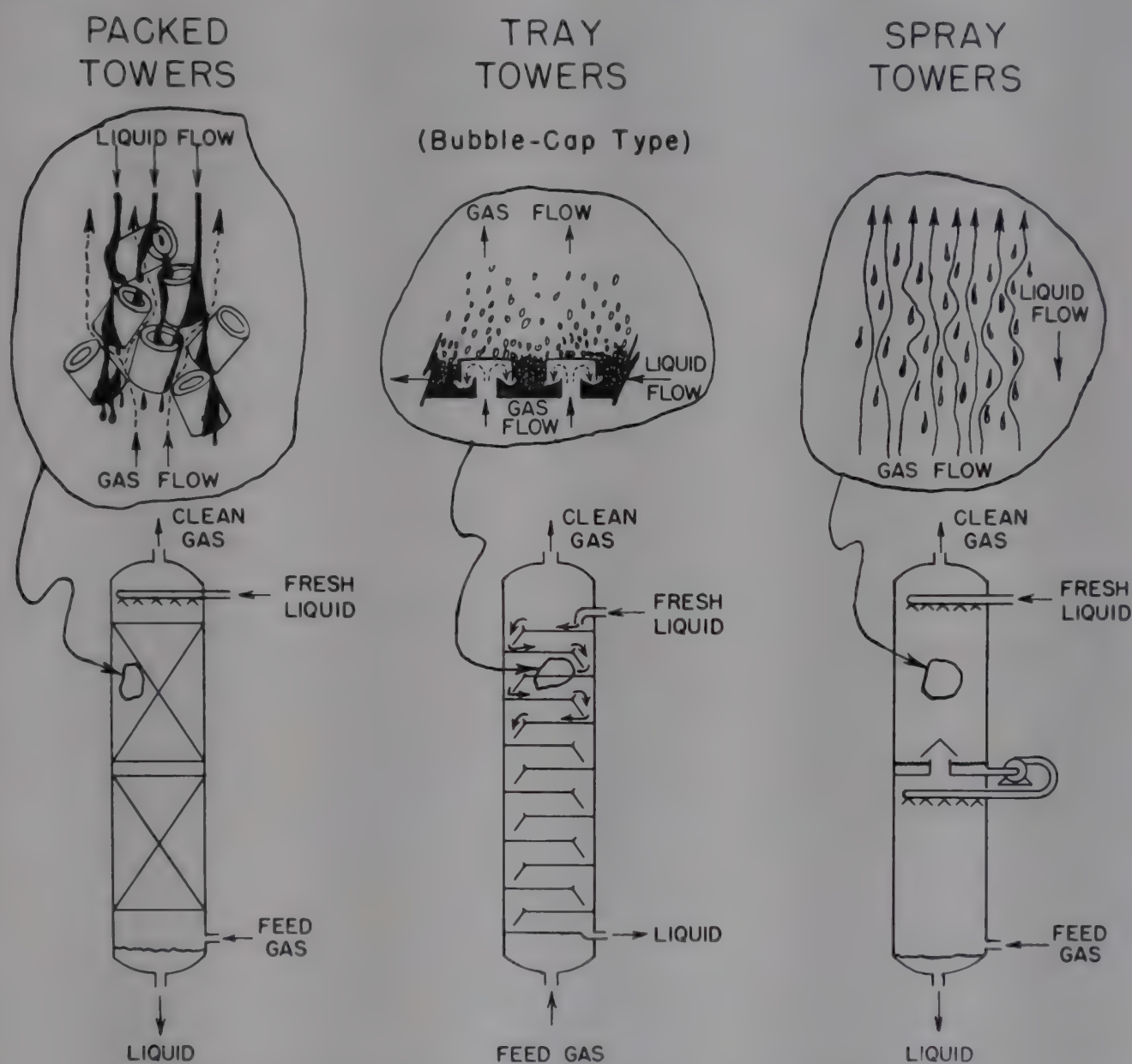


Fig. 1. Operating contact principles of packed, tray, and spray towers.

In perforated-plate towers the upflowing gas is bubbled through the liquid through a multitude of small holes in each plate. In bubble-cap towers the gas passes up through small tubes or chimneys over which are placed inverted cups (or caps) having serrated edges. Gas passes up through the tubes, makes a 180° turn to pass under the cap, and bubbles out into the tray liquid from under the serrated periphery. In spray towers the liquid surface is extended by forcing the liquid through spray nozzles, thus forming a multitude of tiny droplets which fall through the rising gas stream. The principles of each of these methods of effecting gas-liquid contact are illustrated in Figure 1. Plate and packed towers are the most common forms for such equipment. Spray

columns, a number of novelty tray designs, and several other specialty devices are used only in very particular instances.

The principal problem in the design of gas absorption columns is the determination of the necessary absorbing liquid flow rate and/or the amount of exposed surface necessary to accomplish the desired degree of absorption. The economics of both packed and plate towers are such that it is generally desirable to keep diameter to a minimum (at the expense of height). The design of these towers is carried out by first determining the necessary volume or number of equilibrium trays and then determining, from the known gas and liquid rates, the minimum column diameter capable of handling these flow rates (thus fixing the column height). Since packed towers are the more popular and classic example of gas absorption equipment, they will be discussed first, followed by the principles of sizing tray towers. The interrelation between packed and tray towers will then be discussed.

Full treatments of absorption are given by Norman (40a), Sherwood and Pigford (56), and Treybal (68).

Packed Towers

The three main approaches to determining required absorption tower packed volume are referred to in terms of the *mass transfer coefficient* (defined by the two-film theory), the *transfer unit*, and *unsteady-state diffusion* (defined by the penetration theory).

MASS TRANSFER COEFFICIENTS (PHYSICAL ABSORPTION)

The process of gas absorption depends on the dissolving of one component of a gas mixture into a liquid upon contact with the liquid surface. For any gas-liquid system the equilibrium relationship between solubility and partial pressure must be known in order to determine equipment operating characteristics since the deviation from equilibrium conditions constitutes the driving force in the absorption process. The fact that an equilibrium exists makes it quite obvious that solute molecules are able to pass across the interface between gas and liquid in either direction. The rate at which equilibrium is established should depend (barring the mixing effects in a flowing system) upon the rate of diffusion of the solute gas through the nonabsorbed gas and through the absorbing liquid. Since essentially uniform concentrations within the bulk liquid and bulk gas at any instant of time (particularly in a flowing system) are assumed, this diffusional rate-governing step in transfer of solute gas between vapor and liquid is taken to exist directly at the gas-liquid interface. In order to explain observed phenomena in terms of a physically conceivable model, Whitman (74) proposed that at the interface there may be considered to exist a thin film of gas and a thin film of liquid (distinct from their respective bulk fluids) within which the principal resistances or rate-determining diffusional-transfer mechanisms are concentrated. Precisely at the interface these two films are at equilibrium.

The two-film concept is illustrated in Figure 2; the liquid concentrations and partial pressures of the absorbed gas, a , at a given instant of time are represented by the curves between x_{a1} and x_{ai} and between p_{ag} and p_{ai} , respectively. With the passage of time in a nonflowing closed system these two curves would become straight horizontal lines as the bulk gas concentration and the bulk liquid concentration reached equilibrium. In a flowing system Figure 2 represents conditions at some countercurrent

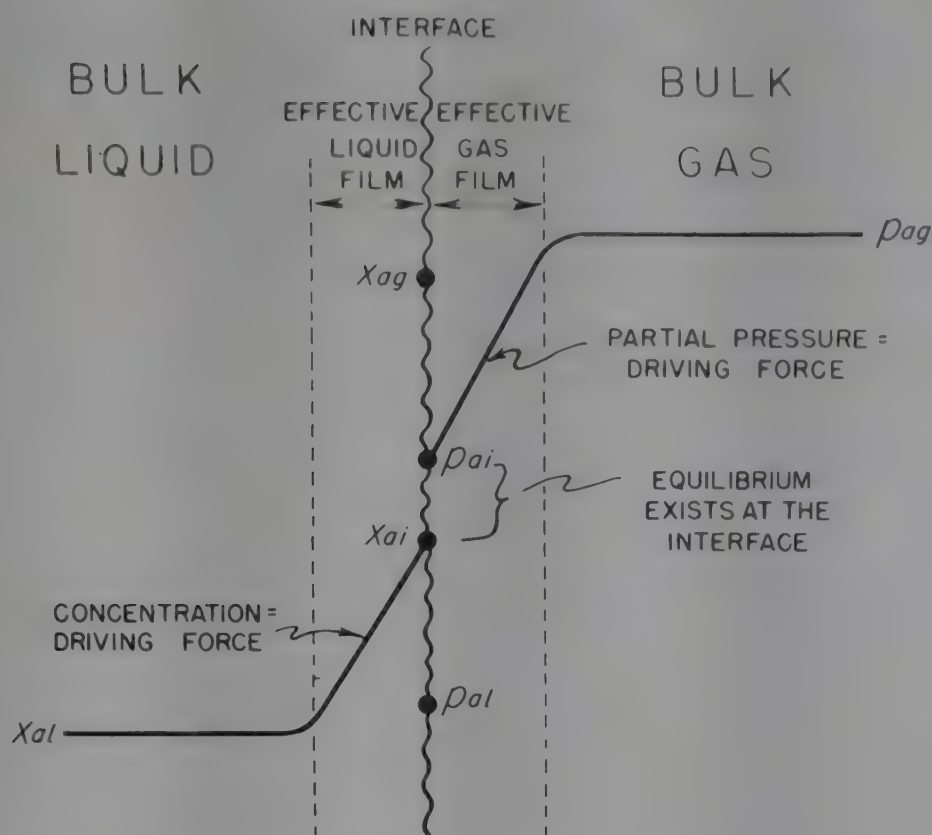


Fig. 2. The two-film concept. NOTE: X_{al} = concentration of a in bulk liquid; p_{al} = equilibrium partial pressure of a in vapor above liquid of concentration X_{al} ; p_{ag} = partial pressure of a in bulk gas; X_{ag} = concentration of a in liquid in equilibrium with gas having partial pressure p_{ag} of a ; X_{ai} = concentration of a in liquid at the interface; p_{ai} = partial pressure of a at the interface.

flow point (eg, at a particular height in an absorption tower) where, as gas and liquid pass each other, the bulk materials do not have sufficient time of contact to attain equilibrium. However, at the exact interface of contact the gas and liquid do attain equilibrium instantaneously and the force potential (and therefore the quantity) with which molecules of solute gas are transferred across the interface during this instant is dependent on the concentration gradients in the films.

The dependence of diffusional flow on concentration gradient is simply a statement of Fick's law (14),

$$\frac{dn}{dt} = Da \left(\frac{dX}{dz} \right) \quad (1)$$

namely that dn , the quantity of material diffusing in direction, z , through an area, a , is proportional to the time interval, the area, and the concentration gradient in the direction of diffusion, dX/dz . The proportionality factor, D , is the diffusivity, or coefficient of diffusion, of the solute material through the bulk fluid. D is inversely proportional to the concentration of the inert material, x_B , in the liquid film through which the material must diffuse. Replacing D with k/x_B , equation (1) may be written

$$\frac{dn}{dt} = \frac{ka}{x_B} \frac{dx}{dz} \quad (2)$$

By integrating across a finite thickness z , with concentration x_{ai} and x_{al} on either side, equation (2) becomes

$$\frac{dn}{dt} = N = \frac{ka}{zx_{BM}} (x_{ai} - x_{al}) \quad (3)$$

where x_{BM} is the log mean concentration of the inert material in the film and N is the amount of material transferred in unit time. The practical application of equation (3) is based on the assumption that z , the film thickness, is a constant, or rather that it represents an effective average value throughout the length of the tower, or contact path. Also x_{BM} is considered as constant since absorption processes involve fairly dilute mixtures and solutions. Equation (3) therefore reduces to

$$N = k_G a (x_{a1} - x_{a2}) \quad (4)$$

or

$$N = k_L a (p_{ag} - p_{al}) \quad (5)$$

Equation (4) expresses the transfer of N molecules of solute through the liquid film and equation (5) the transfer of the same number of molecules of solute through the gas film. The product $k_G a$ is generally expressed in the units of pound moles transferred per hour per cubic foot of bulk packed volume per atmosphere difference in partial pressure of the solute gas and $k_L a$ as pound moles per hour per cubic foot per (pound mole/cubic foot) concentration difference of the solute gas in the absorbing liquid.

The overall absorption occurring in a given tower operating at a total pressure of P atmospheres may be expressed in terms of equation (5) as

$$N = K_G a P (y_{ag} - y_{al})_{\text{mean}} \quad (6)$$

with reference to the notation of Figure 2, where y_{ag} and y_{al} are concentrations expressed in volume or molar fractions rather than partial pressures. When G equals the pounds of total gas flow per hour per square foot of absorption tower free cross-sectional area, M equals the molecular weight of the total gas stream (essentially the inert nontransferred gas), H equals the height of the packed volume, and P equals the total pressure in atmospheres, N may be written as

$$N = \frac{G(y_{a1} - y_{a2})}{MH} \quad (7)$$

in instances when the amount absorbed is a small proportion of the total flow. Using the more common notation y^* to represent the equilibrium concentration, y_{al} , in the gas above a liquid, and letting $y = y_{ag}$ for simpler notation, equations (6) and (7) may be equated and solved for $K_G a$.

$$K_G a = \frac{G}{MPH} \int_{y_1}^{y_2} \frac{dy}{y - y^*} \quad (8)$$

It will be noted that in the derivation of this relationship, equation (6) treated the driving force as occurring across a composite of both the gas and liquid films. Thus $K_G a$ represents an overall coefficient of mass transfer expressed in terms of the gas composition. This overall coefficient can be broken down into its component liquid- and gas-film resistances by referring again to Figure 2. At the interface it is assumed that the two films are in equilibrium so that from equations (4) and (5)

$$N = k_L a (x_{a1} - x_{a2}) = k_G a (p_{ag} - p_{al}) \quad (9)$$

If the assumption is made that the equilibrium relationship may be represented by a straight line of slope m so that $x_a = mp_a$, then from equation (9)

$$N = mk_L a (p_{at} - p_{al}) = k_G a (p_{ag} - p_{al}) \quad (10)$$

As defined by equation (6) the overall coefficient is expressed in terms of the bulk fluid concentrations as

$$N = K_G a (p_{ag} - p_{al}) \quad (11)$$

so that in terms of equation (10)

$$K_G a = \frac{1}{(1/k_G a) + (1/mk_L a)} \quad (12)$$

Combining equations (8) and (12) and solving for tower height, H , gives

$$H = \frac{G}{MP} \left[\frac{1}{k_G a} + \frac{1}{mk_L a} \right] \int_{y_2}^{y_1} \frac{dy}{y - y^*} \quad (13)$$

Equation (13) is based on operation at constant temperature and constant pressure, with the solute gas only a small fraction of the total gas stream, and with the equilibrium curve nearly a straight line of slope m . The equilibrium curve is most commonly represented as y^* , rather than p , versus x . If the equilibrium curve is not a straight line, as illustrated in Figure 3, then m is no longer a constant and must be included under the integral so that equation (13) becomes

$$H = \frac{G}{MPk_G a} \int_{y_2}^{y_1} \frac{dy}{y - y^*} + \frac{G}{M\rho_M k_L a} \int_{y_2}^{y_1} \frac{dy^*}{dx} \frac{dy}{y - y^*} \quad (14)$$

where $dy^*/dx = m_x$, the point value of m (slope of equilibrium curve) at the composition x .

In most practical instances the solute gas concentrations are low and Henry's law (vapor pressure directly proportional to concentration) (47) may be assumed to apply. This gives a straight line for the equilibrium curve, as shown in Figure 3. It is customary to plot an operating line, as also shown in Figure 3, in which each point represents a solute concentration in the gas stream and a solute concentration in the liquid stream for a certain point throughout the height of the tower. The operating line is obtained by a material balance.

$$\underbrace{(\text{lb moles out}) - (\text{lb moles in})}_{\text{Solute in liquid stream}} = \underbrace{(\text{lb moles in}) - (\text{lb moles out})}_{\text{Solute in gas stream}}$$

$$\frac{Lx_1}{M_L} - \frac{Lx_2}{M_L} = \frac{G}{M} \frac{p_1}{P} - \frac{G}{M} \frac{p_2}{P} \quad \text{or} \quad \frac{L}{M_L} (x_1 - x_2) = \frac{G}{M} (y_1 - y_2)$$

For known solute concentrations in the entering gas stream and the leaving liquid stream, fixing the ratio of L/G gives a relationship between solute concentrations in the gas and liquid streams at any other point up the column. The above equation thus defines the operating line shown in Figure 3. In the usual case where the operating line can be taken as straight (eg, column pressure drop negligible relative to the total pressure, solute concentration in feed gas stream relatively low, and essentially isothermal operation without condensation or evaporation of other components) it can be

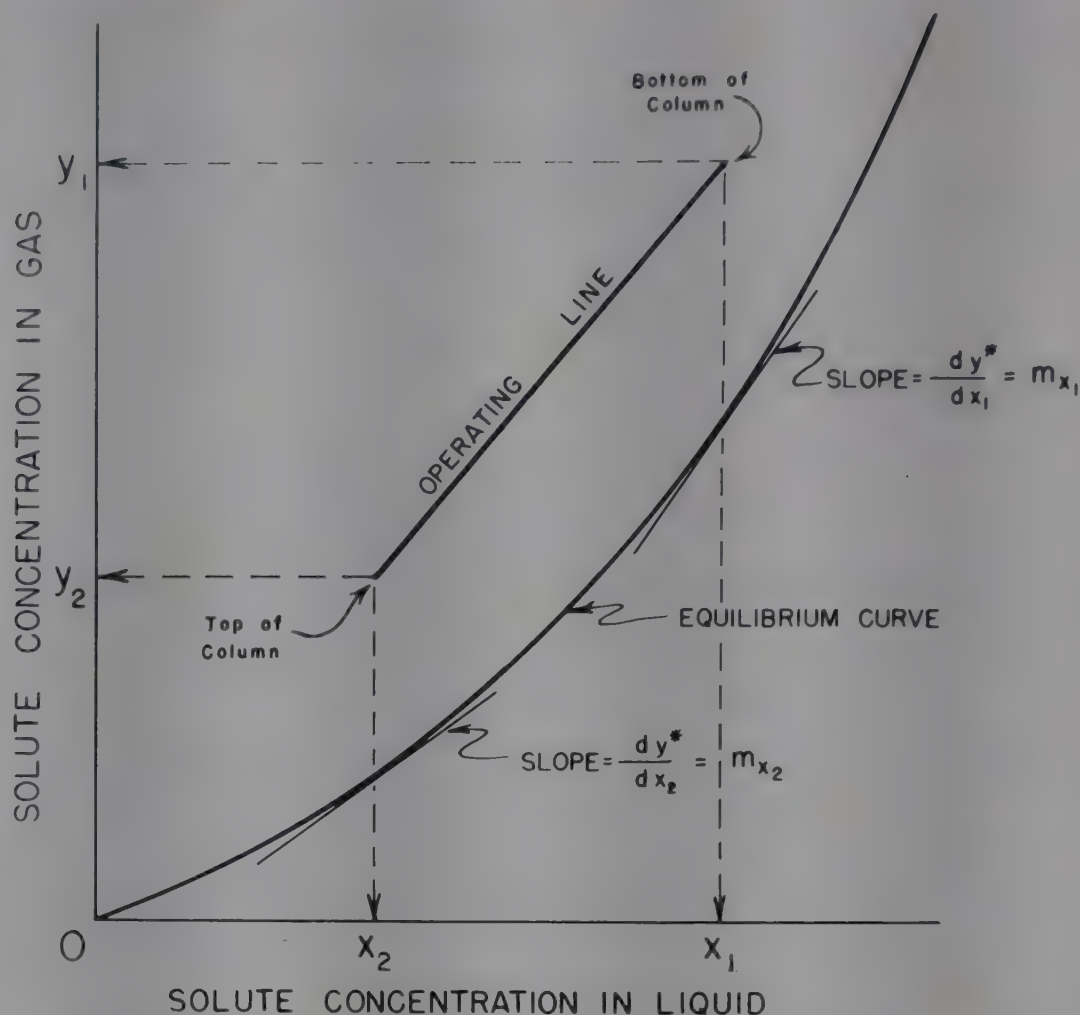


Fig. 3. Typical equilibrium curve and operating line in countercurrent absorption.

shown that the integral in equation (13) can theoretically be represented by the log mean of the driving forces at the top and bottom of the countercurrent contacting column. This obviates the graphical integration and yields the simple relation

$$H = \frac{G(y_1 - y_2)}{MP} \left[\frac{1}{k_G a} + \frac{1}{m k_L a} \right] \frac{(y - y^*)_1 - (y - y^*)_2}{\ln [(y - y^*)_1 / (y - y^*)_2]} \quad (15)$$

where y is the mole fraction solute gas in the total gas stream and y^* is the mole fraction of solute gas which would be in the total gas stream if the stream were in equilibrium with the liquid at that point. The subscripts 1 and 2 refer respectively to the bottom of the tower (where feed gas enters and absorbing liquid leaves) and to the top of the tower (where fresh absorbing liquid enters and scrubbed gas leaves).

When a system obeys the conditions necessary for equation (15) to apply, the values of the individual coefficients $k_L a$ and $k_G a$ are essentially impossible to compute from experimental data. The individual coefficients are obtained from experiments with systems known to have either a negligible liquid-film resistance (eg, highly soluble gases, ammonia-water system, etc) or a negligible gas-film resistance (eg, the oxygen-water system). Presumably, if sufficient data were accumulated and could be correlated with the physical properties of the gases and liquids, as well as their respective flow rates and other parameters, then a means of predicting both film coefficients could be established for any new system or operating condition being considered. The equilibrium partial-pressure solubility data (or Henry's law constant) would also have to be known or estimated (47). Then by means of equation (13), (14), or (15) the necessary tower height or packed volume could be calculated. Other variations of

equations (13) through (15), for particularly shaped equilibrium relationships and for cases where the quantity of solute gas is so great as to affect the total gas flow and hence the operating line, have been explored at length to devise analytical solutions to eliminate the otherwise necessary graphical integration (6,50,51).

The correlation of liquid- and gas-film mass transfer coefficients has never been very successful and it is quite common in practice to employ rather large safety factors in calculations on totally new systems for which no experimental data exist. One of the greatest difficulties in correlation is the fact that the contact surface area is not determinable and in calculations only the total dry surface area of the particular packing material can be employed. Although this can be expected to approach or be relatively proportional to the actual or true contact area it is obvious that (1) for small-size packings and for viscous liquids, or high liquid rates, many interstitial passages are likely to be blocked and unavailable for contact, (2) for large-size packings and particularly low liquid rates the packing may not be fully wetted and therefore a good deal of packing surface be wasted, (3) in large-diameter towers there is greater opportunity for liquid channeling and general maldistribution of flows which is again reflected in loss of effective contact area. However, the available experimental data do follow some patterns which allow reasonable film coefficient estimates, which are usually sufficient for design purposes.

In many instances investigators have found that their data correlate quite well on the basis of some empirical relationship quite distinct from the foregoing formalized treatment and that these relationships are quite useful in design work for the particular system studied. Such relationships are shown in Table 2 along with other pertinent data pertaining to the reported experimental studies. The data of these investigators are also shown in terms of k_G and k_L in Figures 4 and 6. The correlants of Figure 4 are based on the dimensionless groups used successfully by Gamson, Thodos, and Hougen (11,16,64,78) in correlating mass transfer data in packed beds of spheres and cylinders (85).

$$J_d = k_G \frac{PM}{G} \left[\frac{\mu_G}{\rho_G D_G} \right]^{2/3} \text{ versus } N_{Re} = \frac{\sqrt{S/\pi} G}{\mu_G}$$

where J_d = mass transfer number, dimensionless

k_G = mass transfer coefficient, lb moles/(hr)(ft²), computed on the basis of total packing surface

P = pressure of nondiffusing, gas atmospheres

M = molecular weight of nondiffusing gas

G = mass flow of gas, lb/(hr)(ft²)

μ_G = gas viscosity, lb/(ft)(hr)

ρ_G = gas density, lb/ft³

D_G = diffusion coefficient of solute gas in nondiffusing gas, ft²/hr

S = surface of individual packing unit, ft²

The curve of Gamson et al. for humidification of air over cylinders and spheres is shown in Figure 4 as a base of reference. Since no liquid flow was involved in Gamson's experiments, the mass transfer numbers obtained should represent, in principle, a set of upper limiting values for the mass transfer obtainable in gas absorption (eg, maximum utilization of total packing surface). Indeed, all of the gas absorption data shown in Figure 4 fall below the curve of Gamson et al. The many reasons for such

Table 2. Mass Transfer Data for Systems Exhibiting Physical Absorption

Solute	Solvent	Packing	Tower Size, in.	Tower diam- eter, in.	Gas rate, G , lb/(hr) (ft ²)	Liquid rate, L , lb/(hr) (ft ²)	Bibliog- raphy reference	Mass transfer coefficients
ammonia	water	rings	1½	12	100-1,000	160-1,100	(12)	$\frac{1}{K_{Ga}} = \frac{1}{0.065G^{0.9} L^{0.39}} + \frac{1}{0.31L^{0.65} m}$
ammonia	water	rings	1	12	100-1,000	160-1,100	(12)	$\frac{1}{K_{Ga}} = \frac{1}{0.036G^{0.77} L^{0.20}} + \frac{1}{0.103L^{0.78} m}$
ammonia	water	rings	1½	12	100-1,000	160-1,100	(12)	$\frac{1}{K_{Ga}} = \frac{1}{0.014G^{0.72} L^{0.38}} + \frac{1}{0.093L^{0.78} m}$
ammonia	water	rings	1	10	55-530	440-2,050	(55)	$K_{Ga} = 0.046G^{0.5} L^{0.4}$
ammonia	water	rings	1	15	100-1,100	1,800-18,000	(38)	$K_{Ga} = 0.027G^{0.90} L^{0.13}$
ammonia	water	saddles	1	15	100-1,100	1,800-18,000	(38)	$K_{Ga} = 0.0132G^{0.66} L^{0.40}$
ammonia	water	saddles	1	18	700	1,500	(53)	$K_{Ga} = 23$
ammonia	water	saddles	1	18	700	1,500	(4)	$K_{Ga} = (\text{constant}) (G)^{0.7} (L)^{0.5}$
ammonia	water	rings	3	16	20-200	500	(31)	$K_{Ga} = 0.122G^{0.8}$
ammonia	water	rings (spiral)	4	16	20-200	500	(31)	$K_{Ga} = 0.135G^{0.8}$
acetone	water	rings	¾	6	203-525	470-1,150	(24)	$\frac{1}{K_{Ga}} = \frac{1}{0.000183G^{0.8} L^{1.024}} + \frac{1}{0.028L^{0.8} m}$
acetone	water	rings	½	6	203-525	470-1,150	(24)	$\frac{1}{K_{Ga}} = \frac{1}{0.000315G^{0.8} L^{0.901}} + \frac{1}{0.028L^{0.8} m}$
acetone	water	rings	¾	10	203-525	470-1,150	(24)	$\frac{1}{K_{Ga}} = \frac{1}{0.000635G^{0.8} L^{0.781}} + \frac{1}{0.028L^{0.8} m}$
acetone	water	rings	1¼	10	203-525	470-1,150	(24)	$\frac{1}{K_{Ga}} = \frac{1}{0.001393G^{0.8} L^{0.596}} + \frac{1}{0.028L^{0.8} m}$

acetone	water	rings	1	10	100-600	100-2,000	(46)	$\frac{1}{K_{Ga}} = \frac{1}{0.0333G^{0.8}} + \frac{1}{0.0435L^{0.95}}$
acetone, methyl ethyl etkone, methyl isobutyl ketone, and methyl <i>n</i> -amyl ketones	water	rings	0.394	4	100-700	150-3,000	(52)	$\frac{1}{K_{Ga}} = \frac{1}{0.307 D_G G^{0.8}} + \frac{1}{599 D_L L^{0.8} m}$
carbon dioxide	water	rings	$\frac{3}{8}$	2.05	58	1,500-11,000	(55)	$K_{Ga} = 0.523L^{0.54} m$
carbon dioxide	water	rings	1	10	57-314	770-9,120	(54)	$K_{Ga} = 0.021L^{0.88} m$
oxygen	water	rings	$\frac{1}{2}$	20	100	400-10,000	(55)	$K_{Ga} = 0.296L^{0.645} m$
oxygen	water	rings	1	20	100	400-10,000	(55)	$K_{Ga} = 0.1013L^{0.773} m$
oxygen	water	rings	$1\frac{1}{2}$	20	230	400-10,000	(55)	$K_{Ga} = 0.0958L^{0.773} m$
oxygen	water	rings	2	20	230	400-10,000	(55)	$K_{Ga} = 0.0789L^{0.773} m$
oxygen	water	saddles	$\frac{1}{2}$	20	100	400-30,000	(55)	$K_{Ga} = 0.217L^{0.7} m$
oxygen	water	saddles	1	20	230	400-30,000	(55)	$K_{Ga} = 0.195L^{0.7} m$
oxygen	water	saddles	$1\frac{1}{2}$	20	230	400-30,000	(55)	$K_{Ga} = 0.185L^{0.7} m$
oxygen	water	rings	1	15	570	3,000-32,000	(39)	$K_{Ga} = 0.120L^{0.76} m$
oxygen	water	saddles	1	15	570	3,000-32,000	(39)	$K_{Ga} = 0.201L^{0.89} m$
oxygen	water	rings	1	4, 14	40-650	1,000-28,000	(70)	$K_{Ga} = 0.124L^{0.76} m$
water	phosphoric acid	rings	1	10	128-566	210-820	(63)	$K_{Ga} = 0.01G$
water	air	rings	0.63			900-6,000	(25)	$k_{cad^2}/D_G = 6.08 \times 10^{-4} (dG/\mu)^{1.8} (U^2/2gd)^{0.31} F^{-0.5}$
water	air	rings	1.38			900-6,000	(25)	$k_{cad^2}/D_G = 6.08 \times 10^{-4} (dG/\mu)^{1.8} (U^2/2gd)^{0.31} F^{-0.5}$
benzene	kerosene	saddles	1	12	0-80	1,000-3,000	(18)	$K_{Ga} = 0.0084G^{0.937}$
trichloroethylene	kerosene	saddles	1	12	0-80	1,000-3,000	(18)	$K_{Ga} = 0.0087G^{0.882}$
chloroform	kerosene	saddles	1	12	0-80	1,000-3,000	(18)	$K_{Ga} = 0.0073G^{0.93}$
carbon tetrachloride	kerosene	rings	1	12	39-217	800-1,600	(45)	$K_{Ga} = 0.0107G^{0.88}$
uranium hexafluoride	oil	rings	$\frac{1}{4}$	3	35-90	1,600-6,000	(33)	$K_{Ga} = 0.033L^{0.8} m$

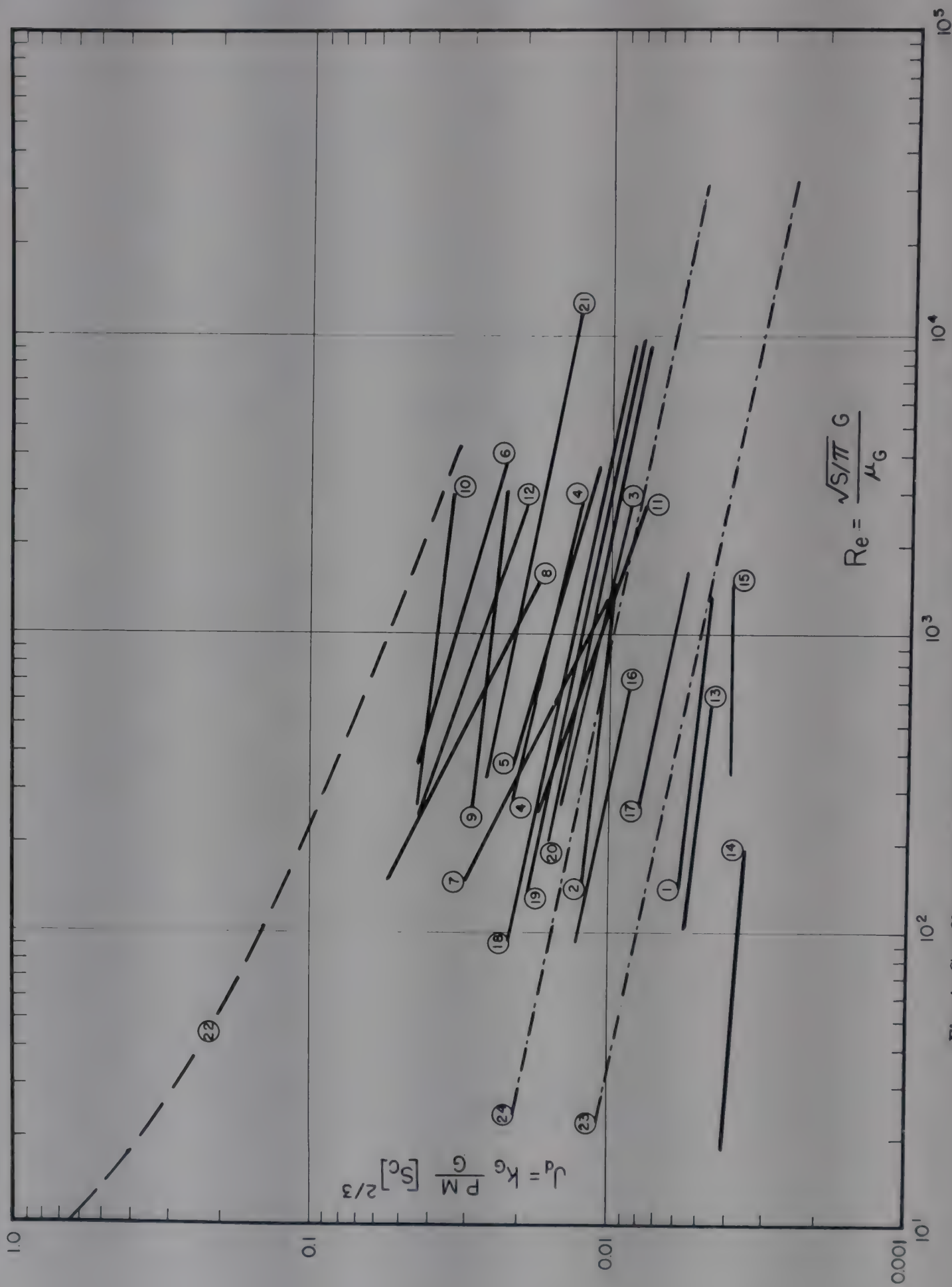


Fig. 4. Gas-film mass transfer coefficients in physical absorption (see also Table 3).

Table 3. Data for Curves Plotted in Figure 4

Curve no.	System	Packing	Size, in.	Liquid rate, L, lb/(hr)(ft²)	Bibliography reference
1	NH ₃ -H ₂ O	rings	½	160	(12)
2	NH ₃ -H ₂ O	rings	½	1,100	(12)
3	NH ₃ -H ₂ O	rings	1	160	(12)
4	NH ₃ -H ₂ O	rings	1	1,100	(12)
5	NH ₃ -H ₂ O	rings	1½	160	(12)
6	NH ₃ -H ₂ O	rings	1½	1,100	(12)
7	NH ₃ -H ₂ O	rings	1	440	(55)
8	NH ₃ -H ₂ O	rings	1	2,050	(55)
9	NH ₃ -H ₂ O	rings	1	1,800	(38)
10	NH ₃ -H ₂ O	rings	1	18,000	(38)
11	NH ₃ -H ₂ O	saddles	1	1,800	(38)
12	NH ₃ -H ₂ O	saddles	1	18,000	(38)
13	CCl ₄ -kerosene	rings	1	800-1,600	(45)
14	C ₆ H ₆ -kerosene	saddles	1	1,000-3,000	(18)
15	H ₂ O-H ₃ PO ₄	rings	1	210-820	(63)
16	ketones-H ₂ O	rings	0.394	150-3,000	(52)
17	acetone-H ₂ O	rings	1	100-2,000	(46)
18	acetone-H ₂ O	rings	⅜	1,000	(24)
19	acetone-H ₂ O	rings	½	1,000	(24)
20	acetone-H ₂ O	rings	¾	1,000	(24)
21	acetone-H ₂ O	rings	1¼	1,000	(24)
22	Humidification of air in sphere- and cylinder-packed towers; Q = 0.				(11,16,64,78)
23	Scheibel's general equation for 10-mm rings; D _G = 0.5; Sc = 1.0.				
24	Scheibel's general equation for 1-in. rings; D _G = 0.5; Sc = 1.0.				

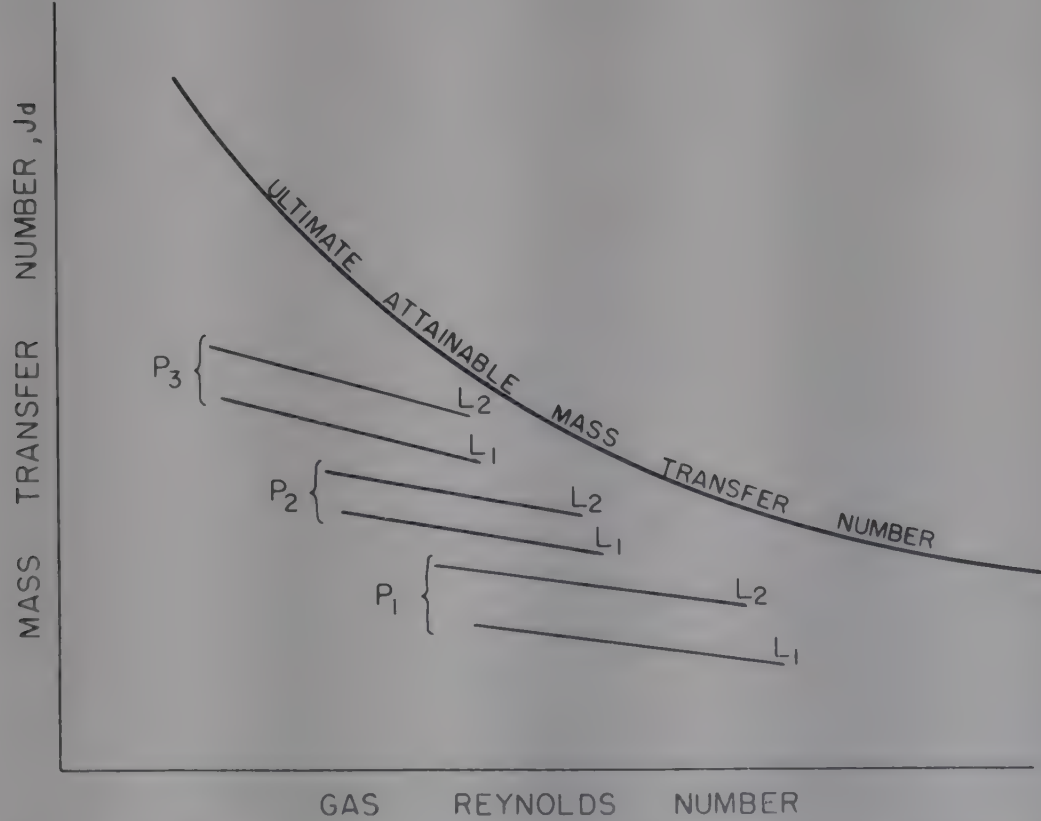


Fig. 5. Schematic illustration of effect of packing diameter and liquid rate on gas-film mass transfer coefficient. P₁, P₂, P₃, . . . P_n indicate increasing packing size. L₁, L₂ indicate increasing liquid down-flow rate.

incomplete utilization of available packing surface area, due to maldistribution of flow, blocking of interstices, incomplete wetting, etc, have been summarized previously. To date no satisfactory correlation of the deviation from the Gamson (100% wetted surface) curve in terms of liquid properties, flow rate, or packing size has been reported; there are indications that such a study could resolve the information in Table 3 which at first glance appears to be a rather disorganized maze of data. In using Figure 4 and Table 3 to estimate k_Ga values it will be noted that the data appear to follow the trends outlined schematically in Figure 5; smaller packing sizes tend to show lower values of J_d ; an increasing liquid rate usually increases J_d and raises it to approach the Gamson curve when the gas Reynolds number is high and channeling is less likely to occur.

Figure 6 and Table 4 represent available data on the liquid-film resistance. The dimensionless correlants used are those suggested by Van Krevelen (70).

$$k_L \left(\frac{\mu_L}{\rho_L g D_L^2} \right)^{1/3} \text{ versus } N_{Re} = \frac{L}{a \mu_L}$$

- where k_L = liquid film transfer coefficient, ft/hr
- μ_L = liquid viscosity, lb/(ft)(hr)
- ρ_L = liquid density, lb/ft³
- g = acceleration of gravity, ft/hr²
- D_L = diffusion coefficient of solute gas in liquid, ft²/hr
- L = liquid rate, lb/(hr)(ft²)
- a = packing surface area, ft²/ft³

The curves of a majority of the investigators cluster sufficiently well to permit estimations of k_L from Figure 6 within reasonable limits of engineering accuracy in this field.

Table 4. Data for Curves Plotted in Figure 6

Curve no.	System	Packing	Size, in.	Bibliography reference
1	NH ₃ -H ₂ O	rings	1/2	(12)
2	NH ₃ -H ₂ O	rings	1	(12)
3	NH ₃ -H ₂ O	rings	1 1/2	(12)
4	acetone-H ₂ O	rings	3/8, 1/2, 3/4, 1 1/4	(24)
5	acetone-H ₂ O	rings	1	(46)
6	CO ₂ -H ₂ O	rings	3/8	(55)
7	CO ₂ -H ₂ O	rings	1	(54)
8	O ₂ -H ₂ O	rings	1/2	(55)
9	O ₂ -H ₂ O	rings	1	(55)
10	O ₂ -H ₂ O	rings	1 1/2	(55)
11	O ₂ -H ₂ O	rings	2	(55)
12	O ₂ -H ₂ O	saddles	1/2	(55)
13	O ₂ -H ₂ O	saddles	1	(55)
14	O ₂ -H ₂ O	saddles	1 1/2	(55)
15	O ₂ -H ₂ O	rings	1	(39)
16	O ₂ -H ₂ O	saddles	1	(39)
17	O ₂ -H ₂ O	rings	1	(70)
18	C ₆ H ₆ -kerosene	rings	1/4	(59)
19	Scheibel's general equation for 10-mm rings; $D_L = 7 \times 10^{-5}$; $Sc = 550$.			
20	Scheibel's general equation for 1-in. rings; $D_L = 7 \times 10^{-5}$; $Sc = 550$.			

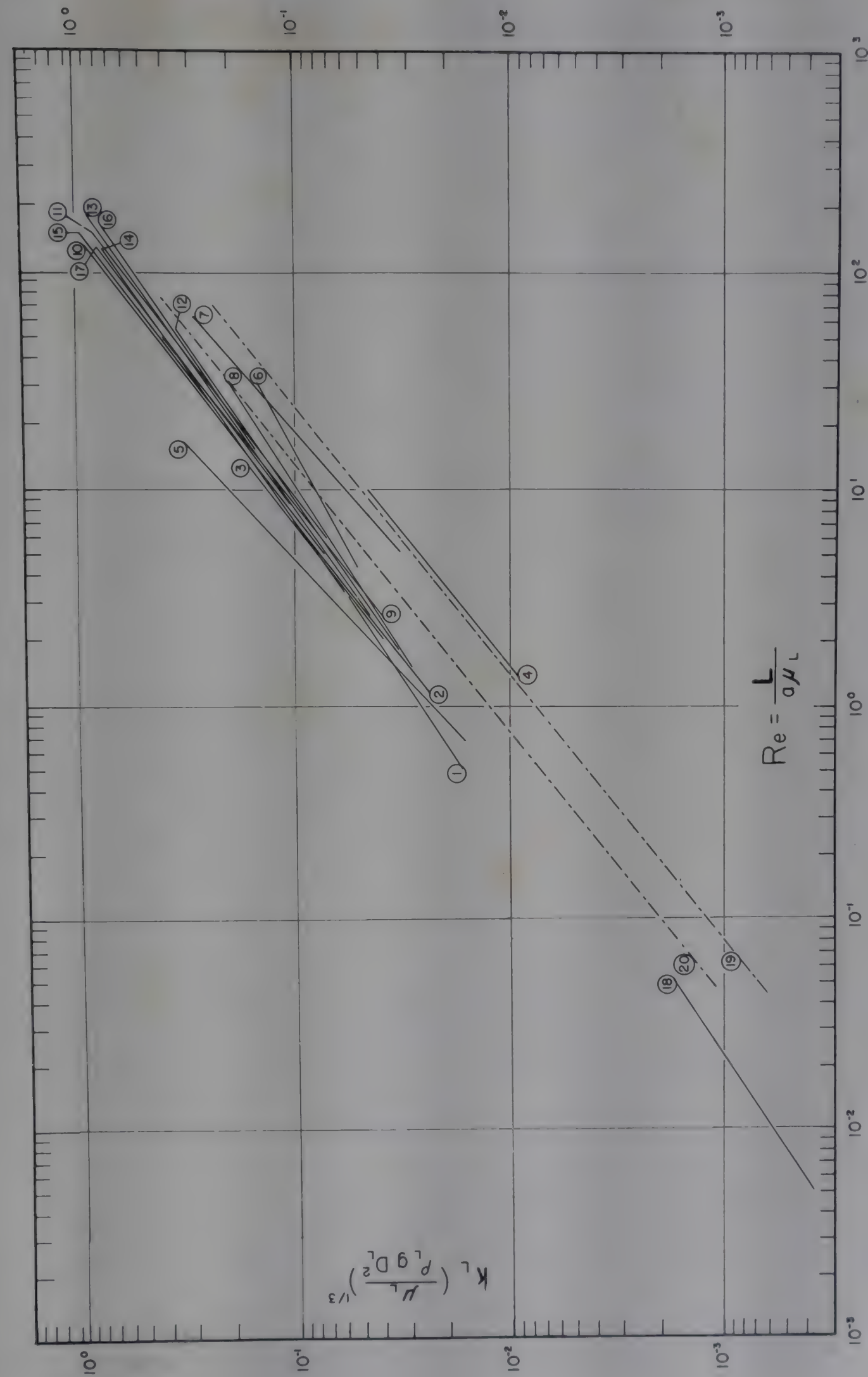


Fig. 6. Liquid-film mass transfer coefficients in physical absorption (see also Table 4).

In conjunction with Figures 4 and 6 values of the diffusion coefficients of the solute gas in the bulk gas and liquid films are necessary, as well as values of the total packing surface per cubic foot of packed volume. Tables 5, 6, and 7 present such values for various systems and packings based on experimental data. In Table 5 the diffusion coefficient, D_G (cm²/sec), is given by

$$D_G = \frac{D_0 \left(\frac{t + 273.2}{t_0 + 273.2} \right)^b}{P}$$

Methods of calculating diffusivities have also been presented in the literature (2,20,77). However, the magnitude of computed values should always be judged in the light of such data as in Tables 5 and 7.

Table 5. Experimental Values of Diffusion Coefficients of Pairs of Gases at Atmospheric Pressure

Gas or vapor	Diffusion coefficient, D_0 (cm ² /sec), into					Temp, t_0 , °C ^a	Temp coeff, b
	Air	CO ₂	H ₂	N ₂	Other gas		
A					Br 0.086		
					He 0.641		1.75
		0.14	0.77	0.20	O ₂ 0.20	20	
air			0.611		O ₂ 0.178		1.75
Br ₂		0.086	0.56		CH ₄ 0.156		
					HCl 0.087		
CCl ₄			0.342			23	
CH ₄	0.196	0.153	0.625				1.75
C ₂ H ₄			0.486		CO 0.116		1.75
C ₂ H ₆			0.459				1.75
CO		0.137	0.651	0.192	O ₂ 0.185		1.75
				0.211		15	
CO ₂	0.138				O ₂ 0.139		2.00
				0.144	N ₂ O 0.096		1.75
			0.550				1.75
			0.619			15	
CS ₂	0.0892	0.063	0.3698				2.00
D ₂			1.21			20	
H ₂	0.611	0.550		0.674			1.75
					O ₂ 0.697	20	
					SO ₂ 0.480	20	
					N ₂ O 0.535	20	
H ₂ O	0.220		0.7516				1.75
		0.1387					2.00
Hg				0.1124			2.00
	0.473					341	
I ₂				0.0654			2.00
N ₂		0.144	0.674		O ₂ 0.181		1.75
NH ₃	0.198		0.604				
CH ₄ O, methyl alcohol	0.1325	0.0879	0.5059				1.75
C ₂ H ₆ O, ethyl alcohol	0.102	0.0685	0.3753				2.00
C ₃ H ₈ O, isopropyl alcohol	0.082						2.00
C ₃ H ₈ O, <i>n</i> -propyl alcohol	0.085	0.0577	0.3153				2.00
C ₄ H ₁₀ O, isobutyl alcohol	0.0727	0.0483	0.2771				2.00
C ₄ H ₁₀ O, <i>n</i> -butyl alcohol	0.071	0.0476	0.2716				2.00

Table 5 (continued)

Gas or vapor	Diffusion coefficient, $D_0(\text{cm}^2/\text{sec})$, into					Temp, $t_0, ^\circ\text{C}^a$	Temp coeff, b
	Air	CO_2	H_2	N_2	Other gas		
$\text{C}_4\text{H}_{10}\text{O}$, <i>t</i> -butyl alcohol	0.087						2.00
$\text{C}_4\text{H}_{10}\text{O}$, <i>s</i> -butyl alcohol	0.074						2.00
$\text{C}_5\text{H}_{12}\text{O}$, <i>n</i> -amyl alcohol	0.0589	0.0422	0.2349				2.00
$\text{C}_5\text{H}_{12}\text{O}$, <i>s</i> -amyl alcohol	0.058						2.00
$\text{C}_6\text{H}_{14}\text{O}$, hexyl alcohol	0.0499	0.0351	0.1997				2.00
C_6H_6 , benzene	0.077	0.0528	0.2948				1.75
C_7H_8 , toluene	0.071						2.00
C_8H_{10} , ethylbenzene	0.0658						1.75
C_8H_{10} , <i>m</i> -xylene	0.059						1.75
C_8H_{10} , <i>o</i> -xylene	0.062						1.75
C_8H_{10} , <i>p</i> -xylene	0.056						2.00
C_8H_{18} , <i>n</i> -octane	0.0505						2.00
C_9H_{12} , cumene, isopropyl- benzene	0.0489						2.00
C_9H_{12} , <i>n</i> -propylbenzene	0.0481						2.00
C_9H_{12} , mesitylene, 1,3,5-tri- methylbenzene	0.056						2.00
C_{10}H_8 , naphthalene	0.0513						2.00
$\text{C}_{14}\text{H}_{10}$, anthracene	0.0421						2.00
$\text{C}_6\text{H}_5\text{Cl}$, chlorobenzene	0.061						2.00
$\text{C}_6\text{H}_7\text{N}$, aniline	0.061						2.00
$\text{C}_7\text{H}_7\text{Cl}$, benzyl chloride	0.066						2.00
$\text{C}_7\text{H}_7\text{Cl}$, <i>m</i> -chlorotoluene	0.054						1.75
$\text{C}_7\text{H}_7\text{Cl}$, <i>o</i> -chlorotoluene	0.059						2.00
$\text{C}_7\text{H}_7\text{Cl}$, <i>p</i> -chlorotoluene	0.051						2.00

^a $t_0 = 0^\circ\text{C}$ except when noted.

Table 6. Characteristics of Common Raschig Ring and Berl Saddle Tower Packing^a

Type	Nominal size, in.	Surface, a , ft^2/ft^3	Design factor, a/F^3
Raschig rings	$\frac{1}{4}$	191	718
	$\frac{1}{2}$	105	592
	$\frac{3}{4}$	72	300
	1	56	160
	$1\frac{1}{2}$	36	105
	2	29	58
Berl saddles	$\frac{1}{4}$	274	4,225
	$\frac{1}{2}$	141	481
	1	78	208
	$1\frac{1}{2}$	50	80

^a These characteristics depend on material (whether metal or ceramic), method of packing, manufacturers' tolerances, etc; the figures in this table are representative of ceramic packing.

Table 7. Diffusion Coefficients for Dilute Solutions of Gases in Liquids at 20°C

Gas	Liquid	D_L , ft ² /hr
CO ₂	water	6.9×10^{-5}
Cl ₂	water	6.2×10^{-5}
H ₂	water	20.2×10^{-5}
HCl	water	2.44×10^{-5}
H ₂ S	water	6.3×10^{-5}
N ₂	water	7.4×10^{-5}
N ₂ O	water	6.8×10^{-5}
NH ₃	water	7.1×10^{-5}
O ₂	water	8.1×10^{-5}
acetone	water	6.24×10^{-5}
benzene	kerosene	5.47×10^{-5}

MASS TRANSFER COEFFICIENTS (ABSORPTION WITH CHEMICAL REACTION)

In instances where the solute gas is absorbed in a liquid or a solution with which it is able to undergo chemical reaction the driving forces become far more complex. Table 8 presents a review of some specific experimental investigations of these systems. The results obtained are shown in terms of the conventional overall mass transfer coefficient defined by equation (12). These coefficients include the reaction effects and should not be used beyond the range of the data on which they were based.

In many instances where a chemical reaction is involved there is essentially zero partial pressure in equilibrium with any solution (ie, $m = 0$) and the liquid-film resistance in the two-film concept is negligible so that $k_G a = K_G a$. This simplification will not hold true in all instances since it is obvious that the relative resistances of the gas and liquid phases in the diffusion mechanism of absorption accompanied by chemical reaction are not only functions of the diffusivities of the solute gas in the vapor and liquid phases, solubility, and contact time, but also of the concentration of unreacted reagent, rate of diffusion of the reagent through the solvent liquid, and the rate of the chemical reaction itself. Much of the past research on absorption with reaction has been difficult to interpret because of lack of knowledge of the mechanism and rate of the reaction and other physicochemical data (10). At the present time a number of institutions are even reinvestigating the hydrodynamics of liquid flow in absorption towers in order to define correctly such basic factors as the interfacial contact area. Whynes (76) showed that the absorption of silicon tetrafluoride gas in water can be explained on the two-film theory even though chemical reaction occurs. Slobodynak (60), Jaymond (26), Kohl (30), and others (35,36) have reported deviations for absorption of sulfur dioxide, nitrogen dioxide, carbon dioxide, and chlorine in water and alkaline and amine solutions. Teller (65) has presented an excellent review of the state of knowledge of absorption with chemical reaction; Olander (43) presented a comparison of results calculated from various theories.

To achieve the maximum economic advantage of absorption when accompanied by chemical reaction, it is desirable that reaction mechanism and reaction kinetics first be determined experimentally. At present there is no universally accepted procedure which permits reliable extrapolation so that the experimentation might just as well be carried out as a simulation of the desired absorption operation. In a commercial process it is economically desirable to select a first-order reaction or attain a pseudo-first-order reaction by using an excess of reagent in the solvent or by using low concentrations of solute gas.

Table 8. Mass Transfer Data for Systems Exhibiting Chemical Reaction During Absorption

Solute	Solvent	Packing	Tower		Gas rate, <i>G</i> , lb/(hr) (ft ²)	Liquid rate, <i>L</i> , lb/(hr) (ft ²)	Bibliography reference	Mass transfer coefficients ^a
			Size, in.	diameter, in.				
SO ₂	H ₂ O	rings	1	6	10-81	1,300-1,505	(27)	$K_{Ga} = 0.415 G^{0.37}$
SO ₂	H ₂ O	rings	1	6	10-81	1,725-1,990	(27)	$K_{Ga} = 0.576 G^{0.37}$
SO ₂	H ₂ O	rings	1	6	10-81	2,330-2,590	(27)	$K_{Ga} = 0.0875 G^{0.95}$
SO ₂	H ₂ O	rings	1	9	625-2,410	1,080	(28)	$K_{Ga} = 0.107 G^{0.95}$
Cl ₂	H ₂ O	rings	1	14	15-60	90-6,700	(75)	$K_{Ga} = 0.0337 L^{0.75} m$
Cl ₂	H ₂ O	rings	1	4	40-650	1,000-28,000	(72)	$K_{Ga} = 0.208 L^{0.6} m$
Cl ₂	H ₂ O	rings	1	14	40-650	1,000-28,000	(72)	$K_{Ga} = 0.156 L^{0.6} m$
CO ₂	1 <i>N</i> NaOH	rings	1/2	6	100-450	800-10,000	(66)	$K_{Ga} = 0.30 L^{0.283}$
CO ₂	2 <i>N</i> NaOH	rings	1/2	6	100-450	800-10,000	(66)	$K_{Ga} = 0.352 L^{0.283}$
CO ₂	2-2.5 <i>N</i> NaOH	rings	3/4	12	333-353	800-6,000	(62)	$K_{Ga} = 0.527 L^{0.20}$
CO ₂	2-2.5 <i>N</i> NaOH	rings	3/4	12	318-348	3,000-15,000	(62)	$K_{Ga} = L^{0.15}$
CO ₂	2-2.5 <i>N</i> NaOH	saddles	1	12	200-500	1,500-9,000	(62)	$K_{Ga} = 0.058 G^{0.35} L^{0.20}$
CO ₂	2-2.5 <i>N</i> NaOH	saddles	1	12	800-1,000	1,500-9,000	(62)	$K_{Ga} = 0.215 G^{0.15} L^{0.20}$
CO ₂	2-2.5 <i>N</i> KOH	rings	3/4	12	311-316	1,400-10,000	(62)	$K_{Ga} = 1.87 L^{0.10}$
CO ₂	0.4 molal K ₂ CO ₃	rings	0.394	3	207-1,141	122-7,540	(7)	$K_{Ga} = 0.001903 L^{0.645}$
CO ₂	0.5 molal Na ₂ CO ₃	rings	3/8	12	40-230	750-6,700	(15)	$K_{Ga} = 0.84 \times 10^{-8} L^{1.18} a^{0.82}/$ (holdup)
CO ₂	0.5 molal Na ₂ CO ₃	rings	1	12	50-430	1,020-6,600	(15)	$K_{Ga} = 0.84 \times 10^{-8} L^{1.18} a^{0.82}/$ (holdup)
CO ₂	0.5 molal Na ₂ CO ₃	saddles	1	12	100-500	1,020-6,900	(15)	$K_{Ga} = 0.84 \times 10^{-8} L^{1.18} a^{0.82}/$ (holdup)
CO ₂	50% soln of di- ethanolamine	rings	0.34	1.4	1.5-6.0	500-1,200	(21)	$K_{Ga} = 0.292 G^{0.825}$
CO ₂	30% soln of mono- ethanolamine	rings	2	11.75	80-120	1,800-4,600	(17)	$K_{Ga} = 0.0173 G^{0.55}$
CO ₂	1,3-diamino-2-pro- panol	rings	2	11.75	160-320	3,100-4,800	(17)	$K_{Ga} = 0.00972 G^{0.55}$
CO ₂	1-4 <i>N</i> diethanol- amine	rings	3/4	8	160-330	980-2,460	(8)	see reference
H ₂ S	NaOH soln, Na ₂ CO ₃ soln, and NH ₄ OH soln	rings	5 mm	30 mm	65	100-1,000	(71)	see reference

^a The relations are as reported by individual investigators and should not be used beyond the limits of the range of variables.

THE TRANSFER UNIT

What has been treated in the literature as a seemingly distinct alternate approach to sizing packed absorption towers, referred to as the transfer unit method, is actually a variation of the mass transfer coefficient approach in which the inaccuracies in correlating $k_G a$ or $k_L a$ are simply invested in the values of the so-called HTU or height of a transfer unit. In its simplest terms the transfer unit approach states that the required height of tower (or depth of packing), H , is equal to the number of transfer units, NTU , times the height of a transfer unit, HTU .

$$H = NTU \times HTU_{OG} \quad (16)$$

The number of transfer units in a given operation was defined by Chilton and Colburn (5) for dilute gas systems as

$$NTU = \int_{y_2}^{y_1} \frac{dy}{y - y^*} \quad (17)$$

which is the extreme right-hand term of equation (13). The tower height, divided by the value from equation (17), representing HTU_{OG} , from equations (12) and (13) is

$$HTU_{OG} = \frac{G}{MPK_G a} \quad (18)$$

In instances where the equilibrium curve is a straight line (Henry's law applies) equation (17) may be expressed analytically in the form

$$NTU_{OG} = \frac{\ln \left[\left(\frac{y_1 - mx_2}{y_2 - mx_2} \right) \left(1 - \frac{1}{L/mG} \right) + \frac{1}{L/mG} \right]}{1 - \frac{1}{L/mG}} \quad (19)$$

where mx_2 represents a gas composition in equilibrium with the entering liquid. If the entering liquid contains no solute gas, then $x_2 = 0$. The solute concentrations in the gas stream, y_1 , and y_2 , represent inlet and outlet conditions, and L and G the total lb mole rates of liquid and gas flow per unit time per unit tower cross-sectional area. Just as the overall transfer coefficient, $K_G a$, is related to the individual coefficients when the equilibrium line is straight, the overall HTU_{OG} is related, by equations (12) and (18), to HTU values for the individual phases. It is not obvious that substitution of experimentally determined $k_G a$ and $k_L a$ values, in order to obtain equivalent HTU 's, would yield correlations bearing significantly less scatter than shown in Figures 4 and 6. Treybal (68) has tabulated, for various packing materials, recommended constants which fit an exponential relationship to the gas- and liquid-phase HTU data of selected investigators.

UNSTEADY-STATE DIFFUSION (PENETRATION THEORY)

Several investigators have suggested that the two-film theory might well be abandoned in favor of a more fundamental or realistic model of the mechanism of absorption. In all instances these other approaches have been based on a picture of turbulence and eddy currents within the bulk liquid bringing fresh masses of liquid to the interface surface, then being replaced, and thus returning to the bulk liquid bearing absorbed gas. It is assumed that at the interface or liquid surfaces these masses instantaneously reach

a composition in equilibrium with the gas phase; thereafter, absorption occurs at a rate corresponding to unsteady-state diffusion from a constant source into an infinitely long medium, decreasing with time, until the particular mass of liquid is replaced with a fresh element brought to the surface by the liquid turbulence. At any instant of time the entire liquid surface may be made up of liquid elements which have been exposed to the gas phase over a wide variety of time periods. The quantitative approach to this theory involves the characterization of the surface age or the rate of surface change. The mean rate of absorption per unit area, N_A , would be the summation, for all ages, of the products of instantaneous absorption rate, $N_A(\tau)$, and fraction of surface having an age τ , or

$$N_A = \int_0^{\infty} N_A(\tau) \cdot \phi(\tau) d\tau \quad (20)$$

where $\phi(\tau)$ represents the distribution function of surface ages.

In order to evaluate N_A Higbie (19) assumed that each surface element is exposed for the same period, θ , before being replaced by a fresh mass of liquid. This led to the relation

$$N_A = 2(x^* - x) \sqrt{D/P\theta} \quad (21)$$

Danckwerts (9), on the other hand, assumed that

$$\phi(\tau) = Ae^{-A\tau} \quad (22)$$

where A is the fractional rate of surface renewal, which led to

$$N_A = (x^* - x) \sqrt{DA} \quad (23)$$

It is interesting to note that each of these two penetration model approaches leads to an apparent variation of k_L with \sqrt{D} whereas equations (1) and (3) for the two-film theory indicate k_L simply proportional to D .

Toor and Marchello (67) suggested that each surface element be considered as having a finite length l . This approach led to the conclusion that the penetration theory would hold if $\tau \ll l^2/D$ and the two-film theory would hold if $\tau \gg l^2/D$. The film and penetration theories would appear to be asymptotes or limiting conditions about this model.

Within the framework of presently available data the results obtained from either the penetration model or the two-film model are essentially identical. The penetration theory might be thought to be more realistic than the two-film theory, but only specifically designed future experiments will resolve or confirm the differences.

In addition to the need for a resolution of the penetration theories and the combined effects of absorption and chemical reaction, and an improved correlation of mass transfer rates, there are a number of gross variables which need better definition. For example, Turner and Hewitt (69) have begun a fundamental study of the amount of inactive liquid held at the point of contact of individual pieces of packing and have related this to the total holdup in a packed bed. Howland (23) and Bloodgood et al. (3) have studied the hydraulics of film flow over packing materials; Saveanu et al. (49) investigated the effects of surface roughness; Norman and Hu (41) explored the wetting characteristics of the packing; Howkins and Davidson (22) have correlated characteristic wave formations on the packing materials; and Shulman (58) and Onda

(44) have reevaluated the question of effective interfacial packing area. Despite the advances which have been made in the science or technology of absorption, it is obvious that the complexities in such a heterogeneous operation leave much of the early work in serious question with regard to inferences of mechanism. As appropriately pointed out by Danckwerts (10), gas absorption depends on the flow of a layer of liquid over discontinuous surfaces and on the generation of gas bubbles at inlet and redistribution grids. Very little is known quantitatively about the mechanism of such flows, but the study of such flow phenomena is essential to an understanding of the true mechanism of absorption. This challenging field still remains open to fundamental discoveries.

PACKED-TOWER DESIGN

The transfer unit or mass transfer coefficient approaches yield, respectively, the packed height or packed volume required for a desired degree and rate of absorption. After a determination of either of these quantities has been made, only the diameter of the packed volume needs to be determined in order to dimension the absorption tower. This diameter is based on a reasonable approach to the minimum diameter, or packed cross section, through which the design gas and liquid rates could flow counter-currently without flooding the tower.

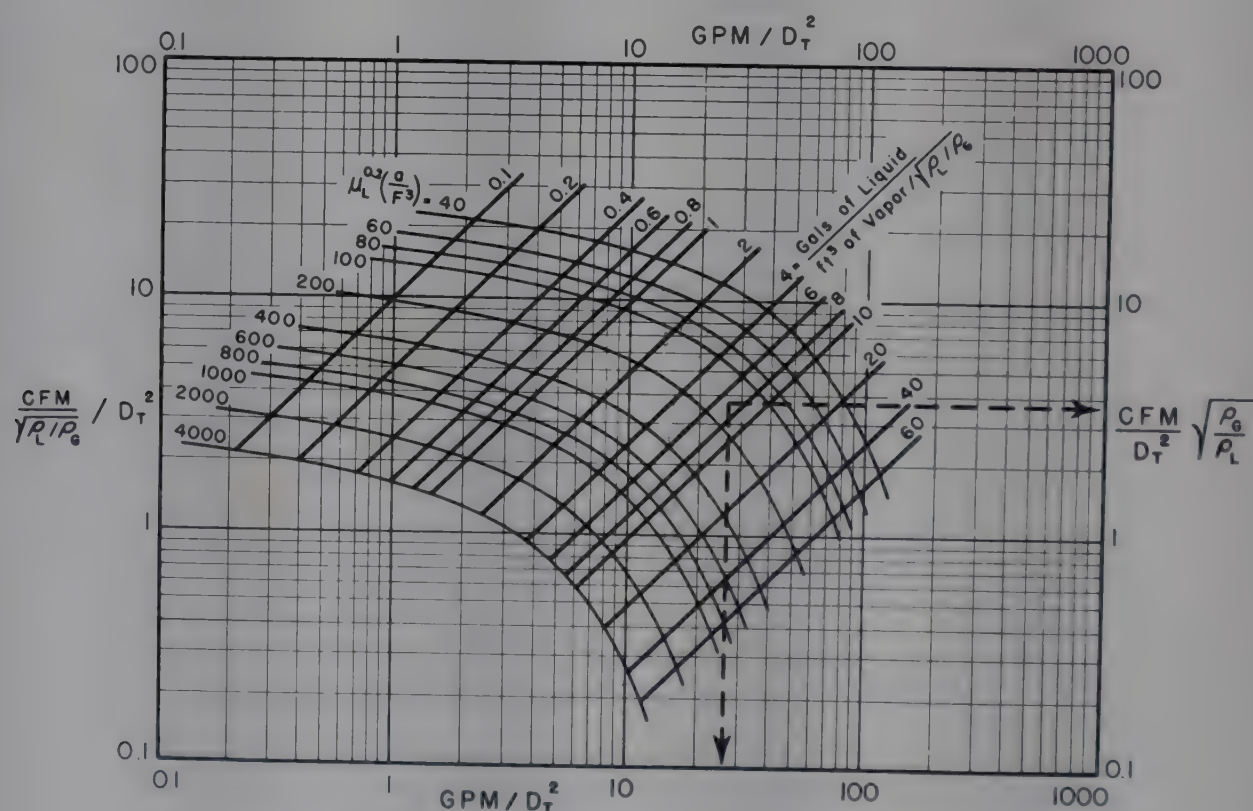


Fig. 7. Design chart for packed-tower flooding rates.

In design work the degree of conservatism, or the nearness of approach to flooding conditions permitted, is a matter of judgment which usually varies with the designer's experience. It is generally accepted that flow rates from 50% to 75% of the flooding flow rate can be permitted. If the operating flow rate is appropriately multiplied by 2, or by $1\frac{1}{3}$, the resulting flooding rate can then be used in conjunction with Figure 7 to calculate the required tower diameter D_T (84). In order to use Figure 7 the packing factor (34), a/F^3 , is obtained from Table 6, and multiplied by the liquid viscosity, μ_L ,

in centipoises raised to the 0.2 power. This product defines one of the parameters which in conjunction with the flow parameter,

$$\frac{\text{gal/min of liquid}}{\text{cu ft/min of vapor}} \sqrt{\frac{\text{liquid density}}{\text{vapor density}}}$$

defines a point on Figure 7 from which either the abscissa or the ordinate determines the tower diameter D_T . Figure 7 merely states that for a given liquid–gas system the relationship between volumetric gas flow and volumetric liquid flow is defined by any one of an empirical family of experimentally determined parallel curves. Each curve represents a different packing material which is characterized by its ratio of surface to cube of void fraction, a/F^3 , per cubic foot of bulk-packed volume. Figure 7 is based on the commonly used randomly dumped Raschig-ring and Berl-saddle type of packings illustrated in Figure 8. A wide variety of other forms of packings, many of which must be stacked rather than simply dumped into the tower shell, are also commercially available and are of interest in very specific instances. Raschig rings may be made of metal, carbon, or ceramic, depending upon the corrosive nature of the system undergoing absorption. Saddle packing is generally ceramic.

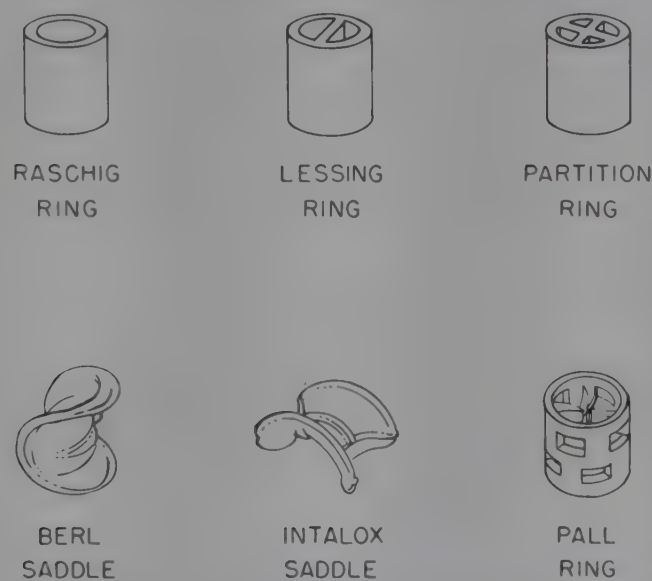


Fig. 8. Random-tower packings.

Gas–Liquid Distribution. Efficient tower operation can be preserved by internal devices for distributing and redistributing the downflowing liquid as well as for establishing good gas distribution at the bottom grid plate. These details bear more directly on the mechanical aspects of tower design than on the theory of the absorption process but are of particular importance in scale-up from small experimental columns.

Large-diameter columns, into which the packing is dumped at random, are usually considerably less efficient than towers of smaller diameter. Analysis of the liquid downflow in a packed column indicates that it will tend to flow to the wall and that the center of the column will become almost dry. The packing will not be very effective because the gas will tend to pass upward through the center of the column. Thus, in large-diameter packed columns provisions must be made for collecting the liquid at the walls and for redistributing it over the packing as uniformly as possible. One method consists of the installation of a trough around the inside periphery of the shell to catch the liquid and to allow it to drain through tubes to different points near the

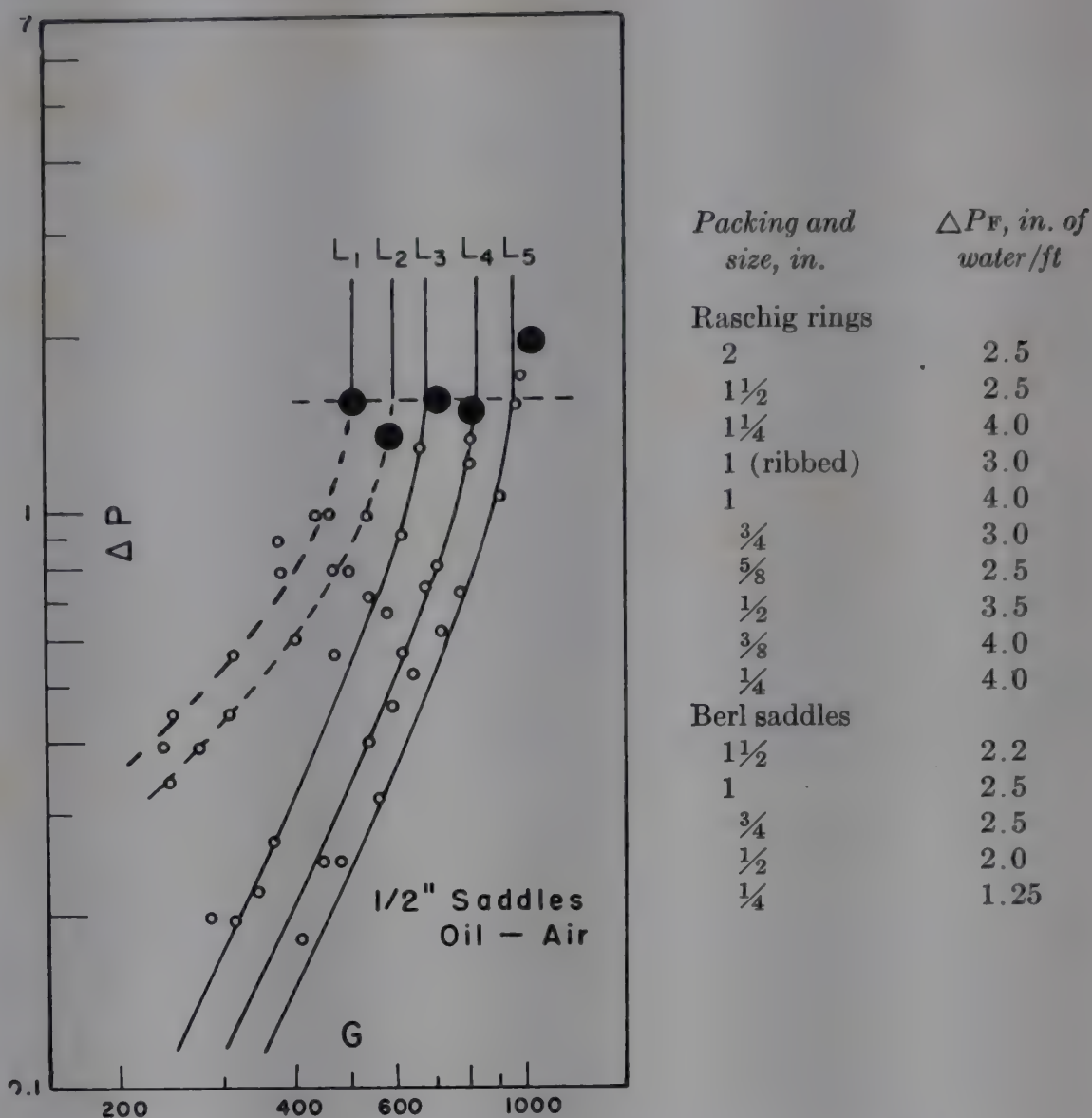


Fig. 9. Typical packed-tower pressure-drop curves showing operation in the gas continuous range (solid line) and the liquid continuous range (dashed line). $L_1 = 3700$, $L_2 = 2950$, $L_3 = 2080$, $L_4 = 1090$, $L_5 = 412$.

center of the packing. This is generally done at 8 to 10 foot intervals, although intervals of 3 to 4 feet are sometimes preferred. It is apparent that under these conditions any economic advantage of a packed column over a plate column, due to simpler construction, might soon disappear. Columns can operate effectively without elaborate redistribution devices when the diameter does not exceed 8 to 12 inches. In general, the packing size should also be less than one eighth of the column diameter. In a packed column greater than 12 inches in diameter the liquid feed at the top should be introduced at several points distributed across the packing level, although a single-point introduction in a 12-inch column will usually only decrease the effect of the top foot of packing depth. To obtain the same results in the plant-scale operation of a large-diameter packed column as in the small laboratory column, the problem of uniform gas and liquid distribution is of the greatest importance in the mechanical design.

Pressure Drop in Packed Towers. Characteristic pressure-drop curves (80) for a packed tower are shown in Figure 9. The horizontal dashed line represents the locus of flooding points above which operation is not possible. The pressure drop at flooding is simply a function of the packing and the kinematic viscosity of the downflowing liquid. The table accompanying Figure 9 presents the values for the gas-pressure drop at the upper break point for a number of packing sizes with water as the

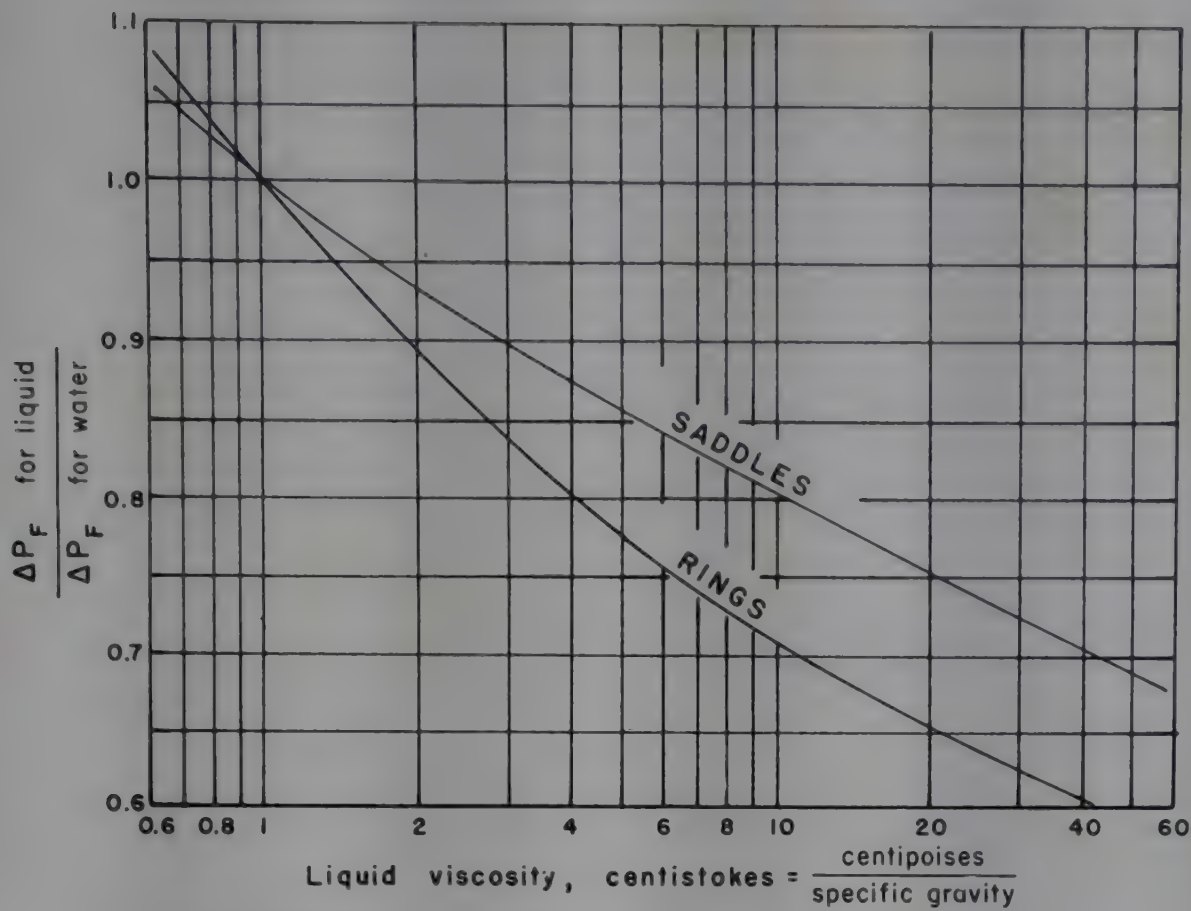


Fig. 10. Pressure drop at flooding for liquids other than water.

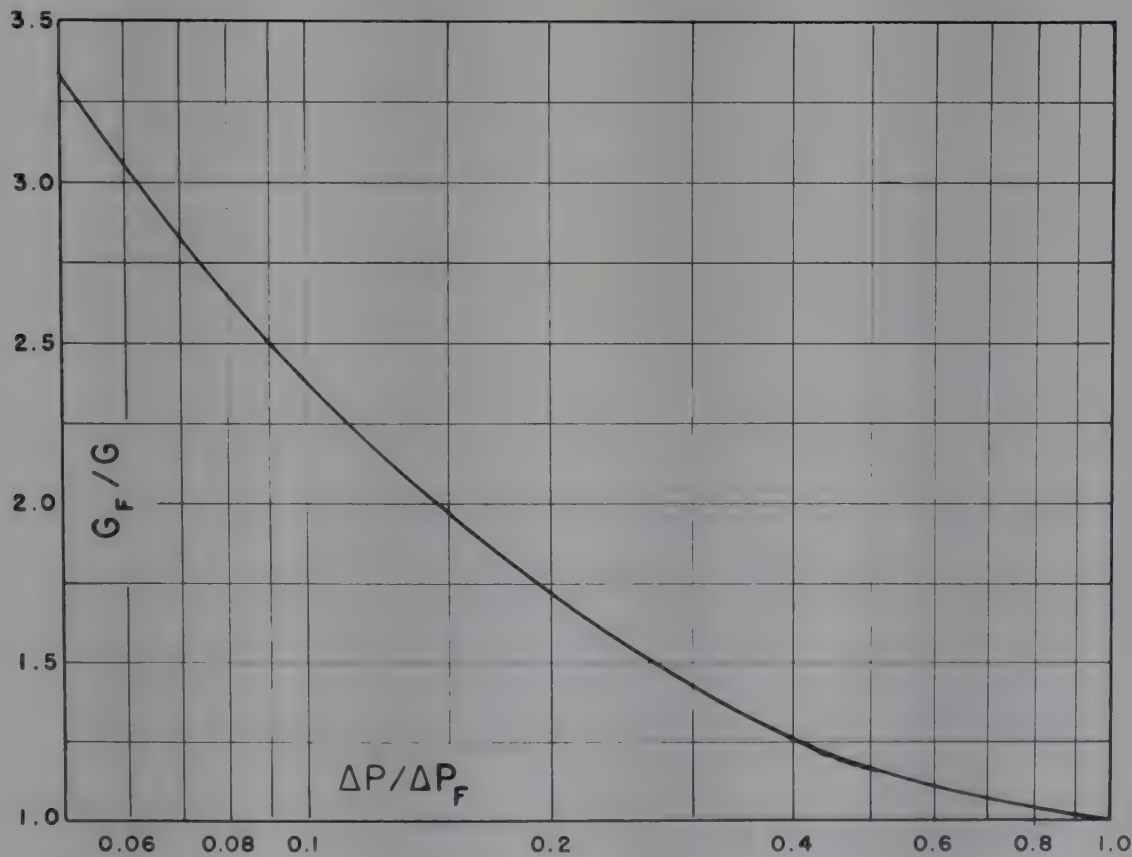


Fig. 11. Correlation of packed-tower pressure-drop curves.

downflowing liquid; Figure 10 gives the effect of liquid viscosity on these values. The pressure drops along any of the parallel solid curves of constant liquid rate in Figure 9 (low liquid rates, referred to as the gas continuous range of operation) are calculable from the gas rate at flooding, G_F , the pressure drop at the flooding point, ΔP_F , and the curve of Figure 11, based on analogy (79) to gas flow through orifices.

The pressure drop along any of the dashed curves of constant liquid rate in Figure 9 (high liquid rates, referred to as the liquid continuous range of operation) can also be calculated from Figure 11 if G and G_F are replaced with L and L_F , and if Figure 9 is cross-plotted as ΔP versus L with lines of constant gas rate, G . The critical liquid rate, L_{LC} , below which tower operation is referred to as being in the liquid continuous range

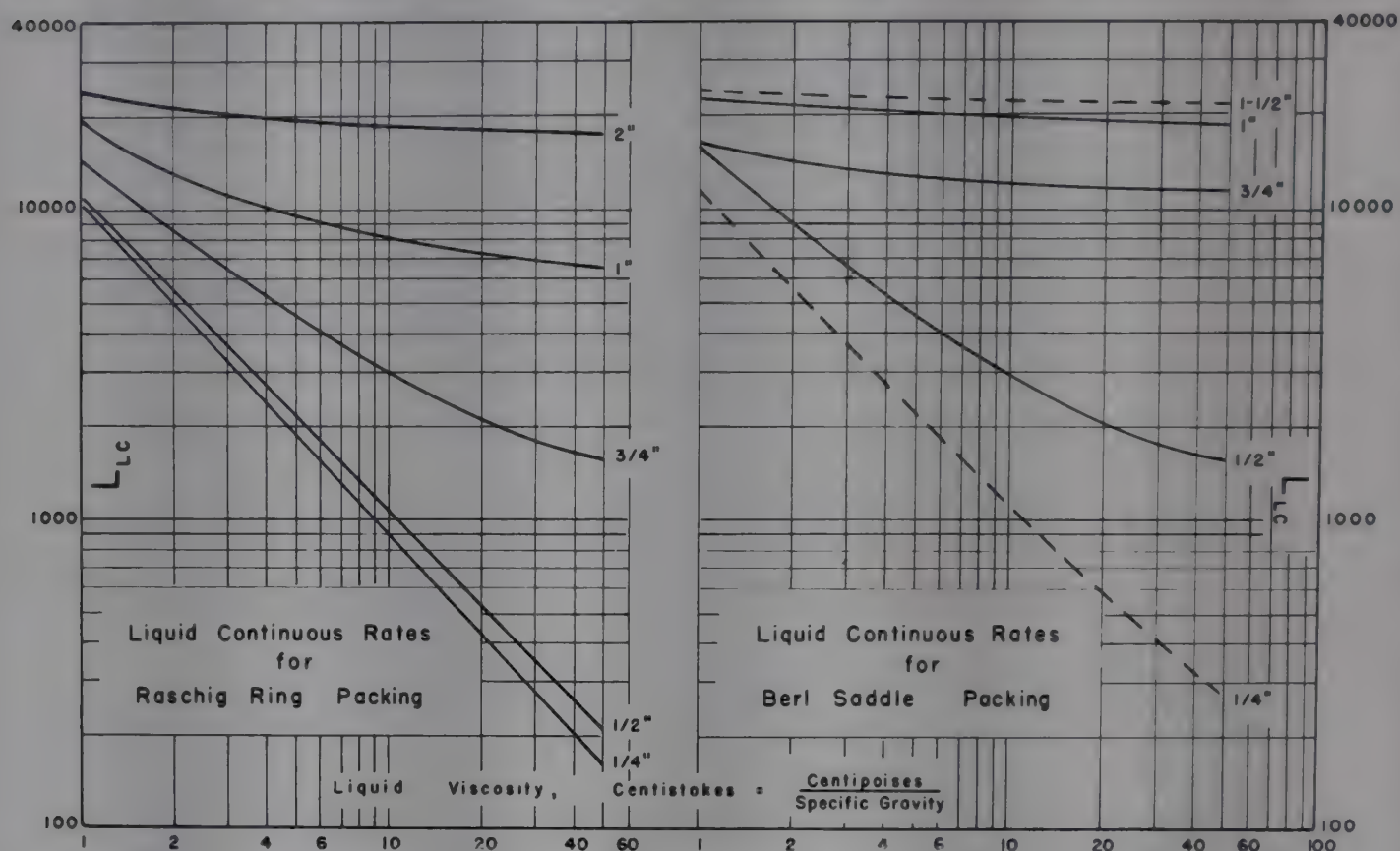


Fig. 12. Liquid continuous rates for ring and saddle packing.

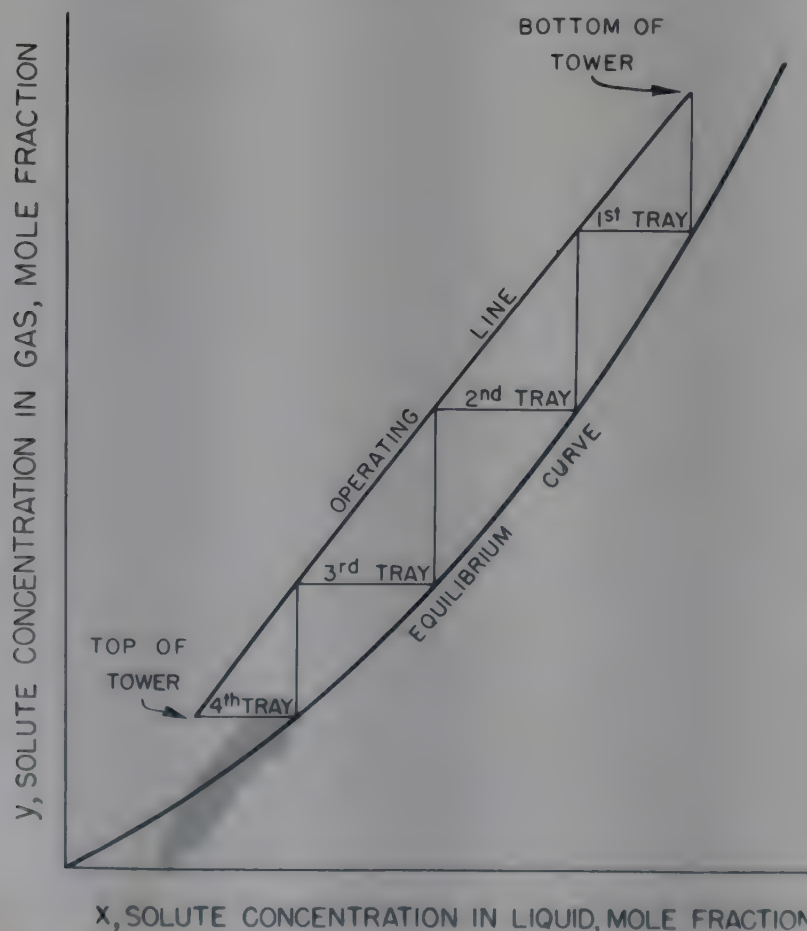


Fig. 13. Graphical determination of number of theoretical trays in an absorption tower.

appears again to be a function of the kinematic viscosity of the downflowing liquid. Such data as can be gleaned from the literature (80) for ring and saddle packings are shown in Figure 12; data in the liquid continuous range of tower operations are much less abundant than data in the gas continuous range. There is also some evidence among certain of the reported mass transfer investigations (57) that L_{LC} represents the minimum liquid rate at which essentially all the packing surface area becomes wetted or effective for gas-liquid contact.

Plate Towers

Number of Theoretical Plates. The design of plate-type absorption towers follows quite generally the procedure used in the design of plate-type distillation towers (see Distillation). In the most general case, the number of theoretical, or 100% efficient, trays can be obtained graphically by stepping off the region between operating and equilibrium curves on a plot such as Figure 3; this is the conventional McCabe-Thiele (37) method as illustrated schematically in Figure 13. The slope of the operating curve is equal to the molar ratio of liquid downflow to vapor upflow; the equilibrium curve is defined from physical-chemical data for the particular system of interest.

As pointed out in the discussion of packed towers, many absorption processes operate in the region of low concentrations where the equilibrium curve is essentially straight (Henry's law). In conjunction with a straight operating line such a case yields to analytical treatment resulting in the Kremser-Brown-Souders equation,

Number of theoretical plates =
$$\frac{\log \left[\frac{y_1 - mx_2}{y_2 - mx_2} \left(1 - \frac{1}{L/mG} \right) + \frac{1}{L/mG} \right]}{\log (L/mG)}$$

(24)

where mx_2 is a gas composition in equilibrium with the entering liquid (32,61). If the entering liquid contains no solute gas, then $x_2 = 0$ and equation (24) can be further simplified. The solute concentrations in the gas stream, y_1 , and y_2 , represent inlet and outlet conditions, and L and G the total lb mole rates of liquid and gas flow per unit time per unit tower cross-sectional area. The quantity L/mG which represents the ratio of the slope of the operating line to that of the equilibrium curve is frequently referred to as the absorption factor in graphical representations of equation (24).

Number of Actual Plates Installed. The actual number of plates required will depend upon the operating efficiency of the installed trays. An estimate of the efficiency can be obtained from the empirical overall efficiency correlation of O'Connell (42) shown in Figure 14 or from the correlation of Walter and Sherwood (73) who gave for integrated point efficiencies of bubble-cap trays the empirically correlated relation

$$E = 1 - 1/\exp \left[h / \left(2.5 + \frac{0.37mM_L}{\rho_L} \right) \mu_L^{0.68} w^{0.33} \right]$$

(25)

- where h = vertical distance from the center of slots to top of weir, inches
- w = width of slot, inches
- m = slope of equilibrium curve
- μ_L = viscosity of liquid, centipoises
- ρ_L = density of liquid, lb/ft³
- M_L = molecular weight of the liquid

If E is considered as the fractional approach to equilibrium, a curve can be drawn between the operating and equilibrium lines in such a way that points B in Figure 15 lie along a curve defined by $AB/AC = E$. The actual number of trays required can then be determined graphically by stepping off increments between the operating line and curve BB . If the operating and equilibrium curves are again both straight, then the actual number of trays, A_c , can be determined analytically by using equation (24), which calculates the theoretical number of 100% efficient trays, Th .

$$A_c = Th \left/ \frac{\log \{1 + E[(mG/L) - 1]\}}{\log (mG/L)} \right. \quad (26)$$

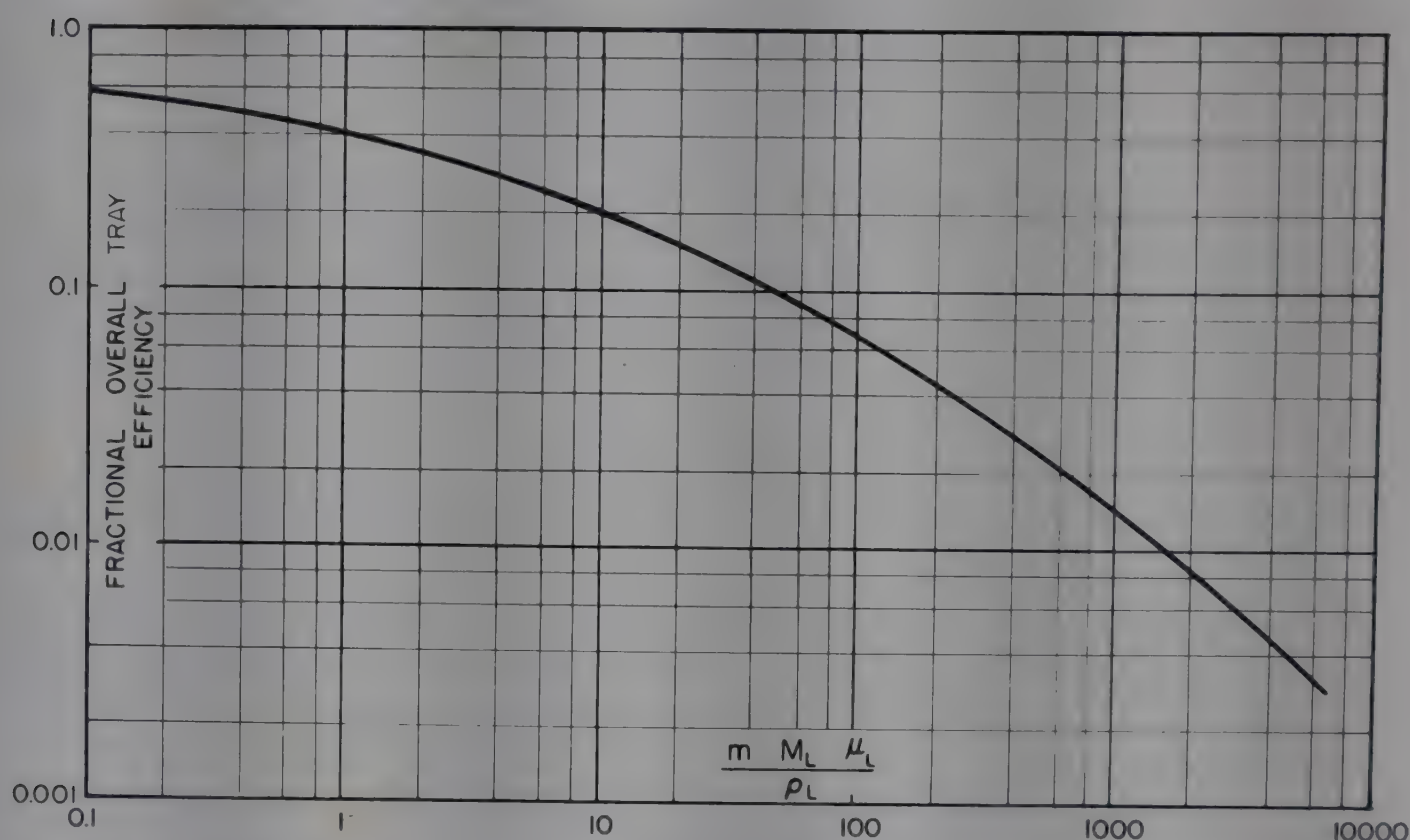


Fig. 14. Overall tray efficiencies of bubble-cap tray absorbers. m = slope of equilibrium solubility curve (mole fraction in gas/mole fraction in liquid); M_L = molecular weight of liquid; μ_L = liquid viscosity, centipoises; ρ_L = liquid density, lb/cu ft.

Tower Height and Diameter. After calculation of the number of plates which must be installed, the height of the tower is determined by the spacing between these trays. The tray spacing is related to the tower diameter since the smaller the diameter the greater the gas-pressure drop and the greater the entrainment of liquid; therefore, the tray spacing is so chosen in order to avoid an excessive loss in efficiency by entrainment and/or to avoid flooding of the downcomers due to increased pressure drop through the trays. Theoretical studies (1,82) have shown that the economic optimum exists under conditions at which the entrainment, expressed as pounds of liquid per pound of gas, is approximately 17.5% of the operating flow ratio L/G . In most instances, however, pressure drop and flooding will limit diameter and tray spacing before the optimum entrainment rate is reached.

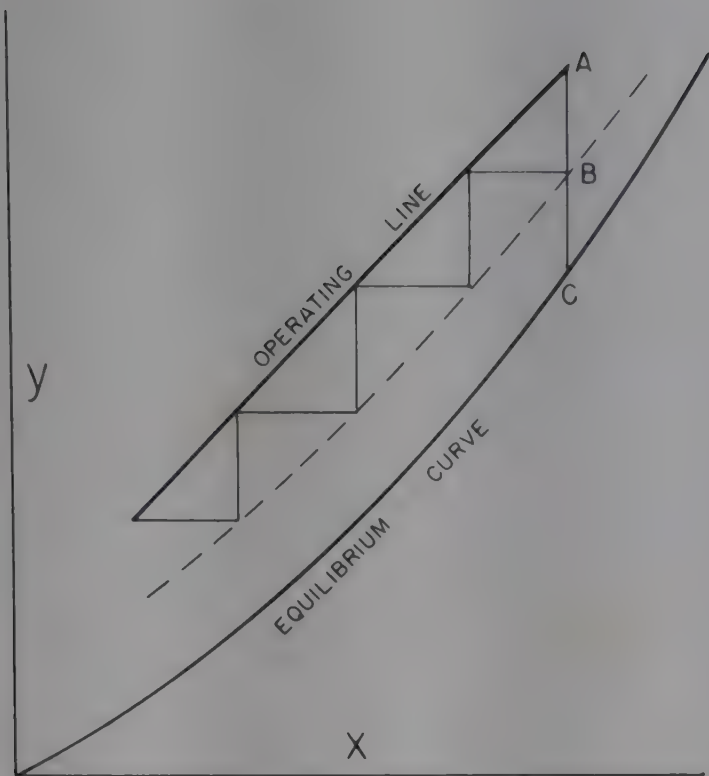


Fig. 15. Graphical illustration of point-tray efficiency.

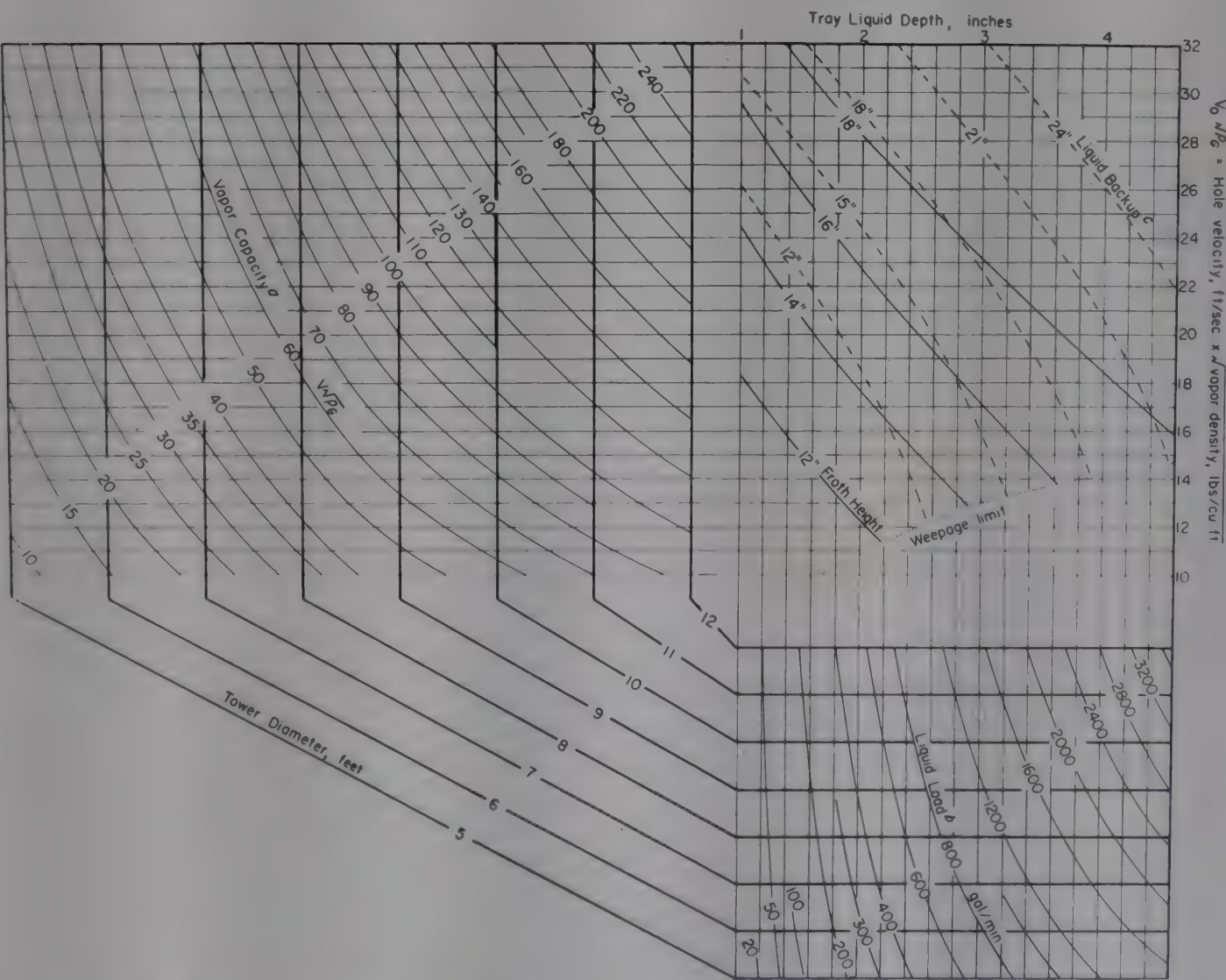


Fig. 16. Perforated-plate-tower sizing chart. Double-flow trays ($\frac{1}{8}$ inch holes on equilateral triangle pitch; 3 holes per inch, 12.7% hole area). ^a Vapor capacity, $V\sqrt{\rho_g} = CFS$ (vapor density, $lbs/cu\ ft)^{1/2}$. ^b Liquid capacity, gallons/minute; Weir height, 1 inch. ^c Liquid backup based on $2 \times$ liquid head (eg, downcomer $\frac{1}{2}$ -full of unaerated liquid).

The literature contains many standard procedures for sizing bubble-cap (83) and perforated-plate (81) trays. Figure 16 illustrates a typical tower sizing chart for a conventional double-flow perforated-plate design. This chart incorporates both entrainment and flooding limitations on the throughput capacity. The solid tray-spacing lines define experimentally measured maximum allowable entrainment limits and the dashed lines define spacings corresponding to twice the pressure drop through the trays expressed in inches of unaerated, or solid, liquid head. The factor of twice the pressure drop is based on a conservative allowance for froth or entrapped gas being carried off the trays into the downcomers. Similar charts for single-flow trays with different hole sizes (usually no more than $\frac{3}{8}$ inch) and hole areas can be drawn on the basis of published data. The use of Figure 16 can be illustrated by considering the case of a tower necessary to handle 800 gallons per minute of liquid downflow and a gas upflow such that $V\sqrt{\rho_G}$, as defined in Figure 16, is equal to 40. A line of constant tower diameter is first selected. This line must intersect these two rates; note that this occurs for the 6, 7, and 8-foot diameter lines. At the point of intersection of the vertical leg of the 7-foot diameter line with the curve for a vapor capacity of 40, a horizontal line is drawn off to the right to its point of intersection with a vertical line drawn upwards from the point at which the horizontal leg of the 7-foot diameter line intersects the curve for a liquid load of 800 gal/min. The two lines so drawn intersect at a point lying on the curve labeled 16 inches which indicates the tray spacing. Froth height or liquid backup, whichever is greater, gives the tray spacing. If this procedure is repeated using a 6-foot tower diameter, it will be found that the point of intersection will call for tray spacing of 21 inches. In general, tray spacings seldom exceed 24 inches unless the absorbing liquid has excessive foaming tendencies, in which case it is advisable to add 6 inches to the tray spacings determined from Figure 16.

Table 9. Vapor-Liquid Capacities of Cross-Flow Trays Provided with 3-Inch Round Bubble Caps^a

Vapor load factor, $V/\sqrt{\rho_L/\rho_G}$	Liquid load, gal/min	Tower diameter, ft	Tray spacing, in.	Type ^b of tray	Number of caps per tray	Weir length, in.	Tray, ΔP , in. of liquid
50-70	31	3	12	SF	26	30	2.7-3.9
	125	3	18	SF	26	30	4.0-5.2
	305	3	24	SF	26	30	5.1-6.3
85-115	42	4	12	SF	43	40	2.7-3.9
	167	4	18	SF	43	40	4.1-5.3
	405	4	24	SF	43	40	5.2-6.4
150-205	84	5	12	DF	78	40	2.7-3.9
	336	5	18	DF	78	40	4.0-5.2
	816	5	24	DF	78	40	5.1-6.3
185-260	104	6	12	DF	98	50	2.7-3.9
	420	6	18	DF	98	50	4.0-5.2
	1020	6	24	DF	98	50	5.1-6.3
275-380	116	7	12	DF	144	56	2.7-3.9
	470	7	18	DF	144	56	4.0-5.2
	1140	7	24	DF	144	56	5.1-6.3
370-520	134	8	12	DF	196	64	2.7-3.9
	538	8	18	DF	196	64	4.0-5.2
	1305	8	24	DF	196	64	5.2-6.4

^a 50% of cap perimeter is slots $\frac{1}{8}$ -inch wide by $1\frac{1}{4}$ -inch long.

^b SF, single-flow tray; DF, double-flow tray.

The sizing of bubble-cap trays is somewhat more complex so that simple graphical presentation is not feasible. On the basis of standard design procedures Table 9 summarizes capacities and design features of some single- and double-flow trays with 3-inch diameter caps. The value of $V/\sqrt{\rho_L/\rho_G}$ and liquid load in gal/min is first computed and then the smallest tower diameter capable of handling these loads is found by scanning the first three columns of Table 9. The corresponding minimum tray spacing, number of caps, weir length, etc, define the principal tray details.

Trays of this type are generally built as single- or double-flow which means that on each tray there is either one inlet and one outlet weir or two inlet and two outlet weirs. The double-flow tray has essentially twice the liquid throughput capacity of a single-flow tray of the same diameter; however, the double-flow tray has less gas capacity since the second weir and downflow arrangement takes some space normally occupied by bubble caps on single-flow trays. Thus double-flow trays may be considered as high L/V trays and single-flow trays as low L/V trays. The principles governing the sizing of bubble-cap or perforated trays to handle a given gas and liquid throughput are independent of the process taking place on the tray and apply equally well for distillation, absorption, humidification, stripping, and other gas-liquid contacting operations.

Packing Height Equivalent to a Tray

In the early stages of packed-tower development it was customary to consider a given packing material as exhibiting a characteristic *HETP*, or height equivalent to a theoretical plate. By this concept the number of 100% efficient theoretical trays necessary for a given performance is calculated as described previously by equation (24) and then multiplied by the characteristic *HETP* for the packing being considered. The characteristic *HETP* values were determined from experimental results by the

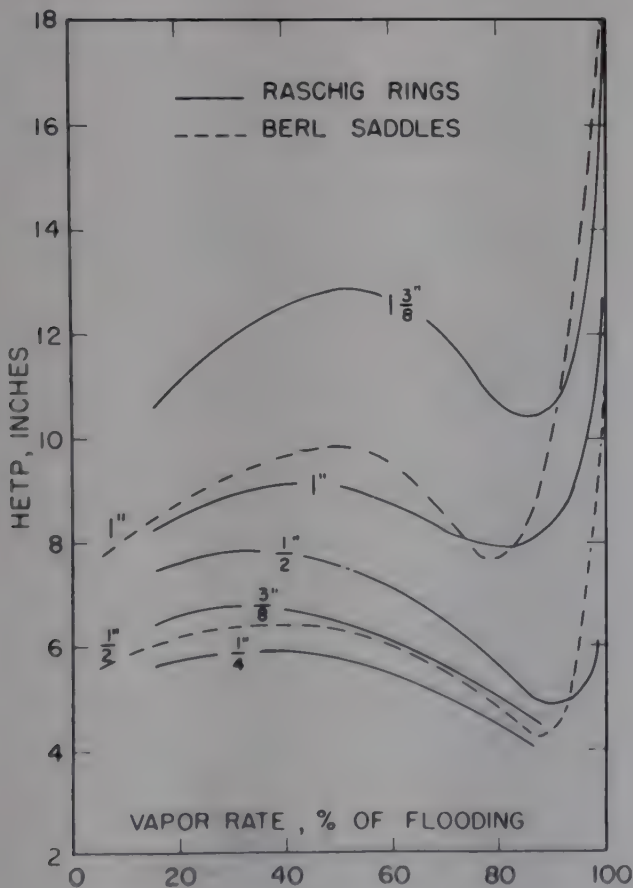


Fig. 17. Generalized comparison of separation performance of various sizes of ring and saddle packing.

reverse procedure. It is obvious from the previous discussions that the *HETP* approach can only be a crude one and certainly not reliable in extrapolation from laboratory to large-scale equipment. However, under certain conditions it can be used as a rapid order-of-magnitude means of estimating the number of trays required if a given packing were replaced, or the packed height required if existing trays were replaced. Figure 17 illustrates typical curves of *HETP* for various sizes of packing plotted as a function of the approach to tower flooding as defined in Figure 7. Figure 17 is based primarily on laboratory scale distillation data (13,29,48) and should not be applied directly to large-scale equipment; *HETP* values as high as 10 feet have been obtained in commercial absorption towers 10 feet in diameter packed with 3-inch Raschig rings.

Nomenclature

A	= fractional rate of surface renewal
a	= film, interfacial, or packing surface area, usually expressed per unit tower volume
a	= absorbed gas
D	= coefficient of diffusion of solute through bulk fluid
D_G	= coefficient of diffusion of a gas through another gas
D_L	= coefficient of diffusion of a gas through a liquid
D_T	= tower diameter
d	= nominal packing diameter
E	= tray efficiency
F	= packing void fraction
G	= mass flow rate of gas
G_F	= gas mass flow rate at the flooding point
g	= acceleration of gravity
H	= tower height
$HETP$	= height equivalent to a theoretical plate
HTU_{OG}	= overall height of a transfer unit based on the gas film
h	= distance from center of bubble-cap slots to top of overflow weir
J_d	= mass transfer number
K_Ga	= overall coefficient of mass transfer based on the gas film
k_Ga	= gas-film mass transfer coefficient, usually expressed as pound moles transferred per hour per cubic foot of tower volume per atmosphere difference in partial pressure of the solute in the gas stream
k_La	= liquid-film mass transfer coefficient, usually expressed as pound moles transferred per hour per cubic foot of tower volume per (pound mole/cubic foot) concentration difference of the solute gas in the absorbing liquid
L	= mass flow rate of liquid
L_F	= liquid mass flow rate at the flooding point
L_{LC}	= liquid flow rate at the transition point where the liquid becomes the continuous phase
l	= finite length
M	= molecular weight of gas stream
M_L	= molecular weight of the liquid
m	= slope of equilibrium curve
m_x	= slope of equilibrium curve at concentration x
N	= amount of material transferred by diffusion in unit time
N_A	= amount of material transferred per unit area
N_{Re}	= Reynolds number
NTU	= number of transfer units
n	= quantity of material diffusing across interface
P	= total pressure or pressure of nondiffusing gas
ΔP_F	= pressure drop at the flooding point
$p = p_{ag}$	= partial pressure of a in bulk gas

p^*	$= p_{al}$	= equilibrium partial pressure of a in vapor above liquid of concentration x_{al}
p_{ai}		= partial pressure of a at the interface
S		= surface area of one packing element
S_c		= Schmidt number
T		= temperature, Kelvin
t		= temperature, Centigrade
U		= superficial gas velocity
V		= volumetric rate of vapor flow
w		= width of bubble-cap slots
X		= concentration
$x = x_{al}$		= concentration of a in bulk liquid
x_{ag}		= concentration of a in liquid in equilibrium with gas having partial pressure p_{ag} of a
x_{ai}		= concentration of a in liquid at the interface
x_B		= concentration of inert material in the liquid film
x_{BM}		= log mean concentration of the inert material in the fluid film
$y = y_{ag}$		= mole fraction of component a in bulk gas
$y^* = y_{al}$		= mole fraction of component a in vapor in equilibrium with bulk liquid
Z		= film thickness
θ		= limited period of time
μ_G		= viscosity of gas stream
μ_L		= liquid viscosity
ρ_G		= density of gas stream
ρ_M		= molar density of liquid
τ		= time
$\phi()$		= function of

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ACACIA. See Diuretics and antidiuretics; Gums and mucilages.

ACAROID, ACCROIDES. See Resins, natural.

ACETALDEHYDE

Acetaldehyde (ethanal, IUPAC), CH_3CHO , is an intermediate in the manufacture of acetic acid, acetic anhydride, butyl alcohol, butyraldehyde, chloral, pyridines, and other derivatives. It is manufactured by the hydration of acetylene, the oxidation or dehydrogenation of ethyl alcohol, and the oxidation of saturated hydrocarbons or ethylene.

Acetaldehyde was first prepared by Scheele in 1774 by the dehydrogenation of ethyl alcohol, and was recognized as a new compound in 1800 by Fourcroy and Vauguelin. Liebig established its constitution in 1835 and named it "aldehyde" from the Latin words translated as al(cohol) dehyd(rogenerated). The formation of acetaldehyde by the addition of water to acetylene was observed by Kutscherow in 1881. Acetaldehyde was first used extensively during World War I as an intermediate for making acetone from acetic acid.

Occurrence. Acetaldehyde is a normal intermediate product in the respiration of higher plants. It occurs in traces in all ripe fruits that have a tart taste before ripening; the aldehyde content of the volatiles has been suggested as a chemical index of ripening during cold storage of apples. Acetaldehyde is an intermediate product of alcoholic fermentation but it is reduced almost immediately to alcohol. It may form in wine and other alcoholic beverages after exposure to air, and imparts an unpleasant taste; the aldehyde ordinarily reacts to form acetal and ethyl acetate. Acetaldehyde is an intermediate product in the decomposition of sugars in the body, and hence occurs in traces in blood. Acetaldehyde is a product of most hydrocarbon oxidations.

Physical Properties

Acetaldehyde is a colorless mobile liquid having a pungent suffocating odor that is somewhat fruity and pleasant in dilute concentrations. Some physical properties of acetaldehyde are given in Table 1, vapor pressure of acetaldehyde and its aqueous solutions in Tables 2 and 3, and the solubility of acetylene, carbon dioxide, and nitrogen in liquid acetaldehyde in Table 4.

Table 1. Physical Properties of Acetaldehyde

formula weight	44.052
melting point, °C	−123.5
boiling point at 760 mm, °C	20.16
density, d_4^{20}	0.7780
coefficient of expansion/°C (0–30°C)	0.00169
refractive index, n_D	1.33113
vapor density (air = 1)	1.52
surface tension at 20°C, dyne/cm	21.2
absolute viscosity at 15°C (cgs units)	0.02456
specific heat, cal/(°C) (g), at 0°C	0.522
at 25°C	0.336
$\alpha = C_p/C_v$ at 30°C and 760 mm	1.145
latent heat of fusion, cal/g	17.6
latent heat of vaporization, cal/g	139.5
heat of solution in water, kcal/mole, at 0°C	−1.96
at 25°C	−1.63
heat of combustion of liquid at constant pressure, kcal/mole	279.2
heat of formation at 273°K, kcal/mole	−39.55
free energy of formation at 273°K, kcal/mole	−32.60
critical temperature, °C	181.5
critical pressure, atm	63.2
dipole moment, Debyes	2.69
ionization potential, ev	10.50
dissociation constant, K_a , at 0°C	0.7×10^{-14}
flash point, closed cup, °C	−38
ignition temperature in air, °C	165
explosive limits of mixtures with air, % acetaldehyde by vol	4–57

Table 2. Vapor Pressure of Acetaldehyde

Temperature, °C	Vapor pressure, mm Hg	Temperature, °C	Vapor pressure, mm Hg
−50	19	20	755
−20	123	20.16	760
0	330	30	1089
5	411	50	2096
10	508	70	3696
15	622	100	7607

The freezing points of aqueous solutions of acetaldehyde are as follows:

Acetaldehyde, % by wt	Freezing point, °C
4.8	−2.5
13.5	−7.8
31.0	−23.0

Table 3. Vapor Pressure of Aqueous Solutions of Acetaldehyde

Temperature, °C	Mole %	Total vapor pressure, mm Hg
10	4.9	74.5
10	10.5	139.8
10	46.6	363.4
20	5.4	125.2
20	12.9	295.2
20	21.8	432.6

Table 4. Solubility of Gases in Liquid Acetaldehyde at 760 mm Pressure

Temperature, °C	Volume of gas (NTP) dissolved in 1 vol acetaldehyde		
	Acetylene	Carbon dioxide	Nitrogen
−16	54		
−6	27	11	
0	17	6.6	
12	7.3	2.45	0.15
16	5	1.5	
20	3		

Acetaldehyde is miscible in all proportions with water and most common organic solvents: acetone, benzene, ethyl alcohol, ethyl ether, gasoline, paraldehyde, toluene, xylenes, turpentine, and acetic acid.

A number of publications are of general interest: vapor pressure data for acetaldehyde and its aqueous solutions (1–3); vapor-liquid equilibria data for acetaldehyde–ethylene oxide (1), acetaldehyde–methanol (4), sulfur dioxide–acetaldehyde–water (5), acetaldehyde–water–methanol (6); the azeotropes of acetaldehyde–butane and acetaldehyde–ethyl ether (7); solubility data for acetaldehyde–water–methane (8), acetaldehyde–methane (9); densities and refractive indexes of acetaldehyde for temperatures 0–20°C (2); thermodynamic data (10–12); pressure–enthalpy diagram for acetaldehyde (13); the specific gravities of acetaldehyde–paraldehyde and acetaldehyde–acetaldol mixtures at 20/20°C vs composition (7); the boiling point vs composition of acetaldehyde–water at 760 mm and the integral heat of solution of acetaldehyde in water at 11°C (7).

The limits and products of the various combustion zones for acetaldehyde–oxygen and acetaldehyde–air have been described in the literature (14–17); the effect of pressure on the explosive limits of acetaldehyde–air mixtures has been investigated by Mitchell and Vernon (18). In a study of the spontaneous ignition of fuels injected into hot air streams, it was found that acetaldehyde was the least ignitable of the aldehydes examined (19,20). The influence of surfaces on the ignition and detonation of fuels containing acetaldehyde has been reported (21,22). Ignition data have been published for the systems: acetaldehyde–oxygen–peroxyacetic acid–acetic acid (23), acetaldehyde–oxygen–peroxyacetic acid (24), and ethylene oxide–air–acetaldehyde (25).

Chemical Reactions

Acetaldehyde is a highly reactive compound exhibiting the general reactions of aldehydes; under suitable conditions the oxygen or any hydrogen may be replaced.

Acetaldehyde undergoes numerous condensation, addition, and polymerization reactions. The important industrial reactions are summarized under Uses, p. 91.

Decomposition. Acetaldehyde decomposes at temperatures above 400°C forming principally methane and carbon monoxide: $\text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO}$. The activation energy of the pyrolysis reaction is 23,350 cal/mole (26). There have been many investigations of the photolytic and radical-induced decomposition of acetaldehyde and of deuterated acetaldehydes (27–29).

The Hydrate and Enol Form. In aqueous solutions acetaldehyde exists in equilibrium with the hydrate, $\text{CH}_3\text{CH}(\text{OH})_2$. The degree of hydration can be computed from an equation derived by Bell and Clunie (30). The mean heat of hydration is -5.10 ± 0.05 kcal/mole; hydration has been attributed to hyperconjugation (31). The enol form, vinyl alcohol, $\text{CH}_2=\text{CHOH}$, exists in equilibrium with acetaldehyde to the extent of approximately 1 molecule per 30,000. Vinyl alcohol has been postulated as an intermediate in the liquid-phase oxidation of ethylene to acetaldehyde (32). Neither the hydrate nor vinyl alcohol has been isolated from the equilibrium mixtures, but certain aldehyde reactions are believed to proceed via these forms.

Oxidation. Acetaldehyde is readily oxidized to peroxy compounds, acetic anhydride, or acetic acid; the principal product isolated depends on the oxidation conditions. Acetaldehyde undergoes autooxidation with air, forming peroxides and peroxyacetic acid (33). Thermal oxidation in the gas phase yields carbon dioxide, carbon monoxide, formaldehyde, hydrogen, hydrocarbons, and peroxy compounds (34–36). Photochemical oxidation of acetaldehyde in the gas phase yields similar products (37,38). In liquid phase oxidation the principal products are peroxy intermediates, peroxyacetic acid, acetic acid, and acetic anhydride (39–42). Oxidation of acetaldehyde with peroxyacetic acid yields acetic acid. Peroxides and peroxyacetic acid have been postulated as intermediates in the oxidation sequence leading from acetaldehyde to acetic acid: $\text{CH}_3\text{CH}(\text{OOH})\text{OOCH}_3$ (43), $\text{CH}_3\text{C}-\text{O}-\text{O}-\text{CHCH}_3$ (44),

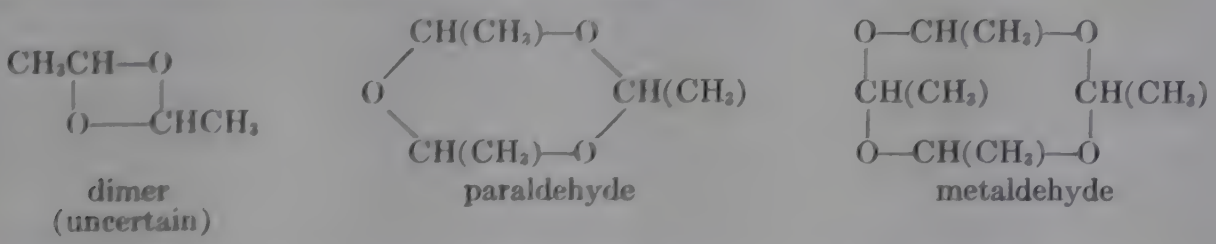
$$\begin{array}{c} | \qquad \qquad \qquad | \\ \text{O} \dots \dots \dots \text{HO} \end{array}$$

and $\text{CH}_3\text{CH}(\text{OH})\text{O}(\text{O}_2)\text{CCH}_3$ (45). The primary product of the oxidation of acetaldehyde by hydrogen peroxide is $\text{CH}_3\text{CHOHOOH}$, which reacts further with the aldehyde (46). When acetaldehyde is oxidized by means of selenium dioxide, glyoxal, CHOCHO , is obtained in good yield (47). Oxidation with atomic oxygen yields a complex mixture of products including biacetyl (2,3-butanedione), formaldehyde, carbon monoxide, carbon dioxide, peroxides, and hydrocarbons (48).

Only liquid phase oxidation of acetaldehyde has been exploited on a commercial scale. Acetic acid is produced by liquid phase oxidation of acetaldehyde at approximately 65°C with a manganese acetate catalyst (49). Liquid phase oxidation of acetaldehyde in the presence of the mixed acetates of copper and cobalt yields acetic anhydride (50). It is believed that peroxyacetic acid or a peroxide are precursors of acetic acid and acetic anhydride. Low-temperature oxidation of acetaldehyde in the presence of metal salts, ultraviolet irradiation, or ozone yields a peroxy intermediate, acetaldehyde monoperacetate, which can be decomposed to peroxyacetic acid and acetaldehyde (51). Peroxyacetic acid can be formed directly by liquid phase oxidation at 40°C with a metal salt catalyst (52). A vapor phase system for the oxidation of acetaldehyde to peroxyacetic acid has been described (53). The oxidation of acetaldehyde in the presence of the acetates of copper and cobalt at 30°C yields diacetyl peroxide $(\text{CH}_3\text{COO})_2$ (54).

Reduction. Acetaldehyde is readily reduced to ethanol. Suitable catalysts for vapor phase hydrogenation are supported nickel (55) and copper oxide (56). Oldenberg and Rose have studied the kinetics of the hydrogenation of acetaldehyde over a commercial nickel catalyst (57).

Polymerization. Acetaldehyde apparently forms a *dimer* which has an odor like acetaldehyde; it is insoluble in water and alkali but soluble in alcohol and benzene (58). When a mineral acid, such as sulfuric, phosphoric, hydrochloric, or sulfur dioxide, is added to acetaldehyde, a *trimer*, *paraldehyde*, is formed (59). In the presence of an excess of concentrated sulfuric acid, tarry condensation products are formed. At lower temperatures with dry hydrogen chloride or pyridine-hydrogen bromide, the *tetramer*, *metaldehyde*, crystallizes from solution (60).



A rubbery polymer of acetaldehyde was discovered in 1936 by Travers (61) and Ietort (62). The polymer is obtained by freezing the pure monomer at approximately -120°C , adding water to the viscous liquid which forms on melting. At one time it was thought that crystallization of the monomer was essential for polymerization (63). It has been found that peroxides are initiators, and water and alcohol co-catalysts for the polymerization reaction (64). More recently it has been shown that a white, nontacky and highly elastic polymer can be formed directly from liquid acetaldehyde using alumina as catalyst at -70°C (65), or by the application of 10,000 atm pressure (66). Crystalline polyacetaldehydes have been prepared using organo-metallic catalysts, such as alkali metal alkoxides (67-70). It has been postulated that the rubbery polymer is produced in cationic polymerization, and the crystalline stereoregulated polymer in anionic polymerization (69).

The evidence indicates that the polymer has the repeating unit $-\text{CH}(\text{CH}_3)\text{O}-$; molecular weights in the range 800,000-3,000,000 have been reported. Polyacetaldehyde is rather unstable; depolymerization is accelerated by the presence of acids or peroxides. The polymers of aldehydes have been discussed in a recent review article by Bevington (71). (See also Acetal resins.)

Reactions with Ammonia and Amines. Acetaldehyde readily adds ammonia to form acetaldehyde-ammonia, $\text{CH}_3\text{CH}(\text{OH})\text{NH}_2$. Diethylamine, $(\text{C}_2\text{H}_5)_2\text{NH}$, is obtained when acetaldehyde is added to a saturated aqueous or alcoholic solution of ammonia and the mixture is heated to $50-75^\circ\text{C}$ in the presence of a nickel catalyst and hydrogen at 12 atm. Pyridine and pyridine derivatives are made from paraldehyde and aqueous ammonia in the presence of a catalyst at elevated temperatures (72); acetaldehyde may also be used but the yields of pyridine are generally lower than when paraldehyde is the starting material. Levy and Othmer have studied the vapor phase reaction of formaldehyde, acetaldehyde, and ammonia at 360°C over oxide catalysts; a 49% yield of pyridine and picolines was obtained using an activated silica-alumina catalyst (73). Brown polymers result when acetaldehyde is reacted with ammonia or amines at a pH of 6-7 and temperature of $3-25^\circ\text{C}$ (74). With acetaldehyde primary amines can be condensed to Schiff bases: $\text{CH}_3\text{CH}=\text{NR}$. The Schiff base reverts to the starting materials in the presence of acids. A number of nitrogen

derivatives are useful in identifying acetaldehyde: the oxime, $\text{CH}_3\text{CH}=\text{NOH}$ (mp 47°C), is formed with hydroxylamine, NH_2OH ; the azine, $\text{CH}_3\text{CH}=\text{NN}=\text{CHCH}_3$ (bp $95\text{--}96^\circ\text{C}$), is the product with hydrazine hydrate, $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$; the phenylhydrazone, $\text{CH}_3\text{CH}=\text{NNHC}_6\text{H}_5$ (mp 57°C), is formed with phenylhydrazine, $\text{C}_6\text{H}_5\text{NHNH}_2$; the semicarbazone, $\text{CH}_3\text{CH}=\text{NNHCONH}_2$ (mp 162°C), is the condensation product with semicarbazide, $\text{NH}_2\text{NHCONH}_2$.

Reactions with Aldehydes and Ketones. The base-catalyzed reaction of acetaldehyde with excess formaldehyde is the commercial route to pentaerythritol, $\text{C}(\text{CH}_2\text{OH})_4$; an aldol condensation of three moles of formaldehyde with one mole of acetaldehyde is followed by a crossed Cannizzaro reaction between pentaerythrose, $(\text{HOCH}_2)_3\text{CCHO}$, the intermediate product, and formaldehyde to give pentaerythritol (75); the process proceeds to completion without the isolation of the intermediate. Pentaerythrose has been made by condensing acetaldehyde and formaldehyde at 45°C using magnesium oxide as catalyst (76). The vapor phase reaction of acetaldehyde and formaldehyde at 300°C over a catalyst composed of sodium hydroxide on silica gel gives acrolein, $\text{CH}_2=\text{CHCHO}$ (77).

In the presence of dilute alkali, acetaldehyde condenses to the dimer, *acetaldol*, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CHO}$, which is an important intermediate in the production of butyraldehyde and 1-butanol (78). Kinetic studies of the aldol condensation of acetaldehyde and deuterated acetaldehydes have shown that only the hydrogen atom bound to the carbon adjacent to the $-\text{CHO}$ group takes part in the condensation reaction and hydrogen exchange (79,80). Acetaldehyde forms aldols with other carbonyl compounds containing active hydrogen atoms. A hexyl alcohol, 2-ethyl-1-butanol, is produced on an industrial scale by condensing acetaldehyde and butyraldehyde in dilute caustic solution followed by hydrogenation of the acrolein intermediate. (See Alcohols, higher, synthetic.) Other examples of aldol condensations involving acetaldehyde are: with acetone, 4-hydroxy-2-pentanone ($\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{COCH}_3$) (81); with benzaldehyde, cinnamaldehyde ($\text{C}_6\text{H}_5\text{CH}=\text{CHCHO}$) (82); with furfural, 2-furanacrolein (82). When acetaldehyde and acetone are passed over an aluminum oxide-ferrous oxide catalyst at 400°C , a mixture containing methyl and ethyl ketones, phenols, xylenols, and resin is formed (83). Condensation of acetaldehyde in the presence of dimethylamine hydrochloride yields polyenals which can be hydrogenated to a mixture of alcohols containing from 4 to 22 carbon atoms (84).

While it is customary to make crotonaldehyde, $\text{CH}_3\text{CH}=\text{CHCHO}$, by dehydration of aldol, it can be made directly by the vapor phase condensation of acetaldehyde, generally over a catalyst (85). A noncatalytic process in which crotonaldehyde is produced by heating aqueous solutions of acetaldehyde to 160°C under a pressure of 450 psi has been described (86).

Ethyl acetate is made commercially by the Tishchenko condensation of acetaldehyde with an aluminum ethoxide or butoxide catalyst (87). The Tishchenko reaction of acetaldehyde with other aldehydes yields mixtures of esters; thus, the reaction of acetaldehyde and butyraldehyde gives ethyl acetate, ethyl butyrate, butyl acetate, and butyl butyrate (88).

Reactions with Alcohols and Phenols. Alcohols add readily to acetaldehyde in the presence of a trace of mineral acid to form acetals; for example, ethanol and acetaldehyde form diethyl acetal, $\text{CH}_3\text{CH}(\text{OC}_2\text{H}_5)_2$ (89). Similarly, cyclic acetals are formed by the reactions with glycols and other polyhydroxy compounds. Mercaptals, $\text{CH}_3\text{CH}(\text{SR})_2$, are formed in a like manner by the addition of mercaptans to acetalde-

hyde. The formation of acetals by a noncatalytic vapor phase reaction of acetaldehyde and alcohol at 350°C has been reported (90). Butadiene can be made by the reaction of acetaldehyde and ethyl alcohol at temperatures above 300°C over a tantalum-silica catalyst (91). Aldol and crotonaldehyde are believed to be intermediates. Butyl acetate has been prepared by the catalytic reaction of acetaldehyde with 1-butanol at 300°C (92).

Reaction of one mole of acetaldehyde with excess phenol in the presence of a mineral acid catalyst gives 1,1-bis(*p*-hydroxyphenyl)ethane, $\text{CH}_3\text{CH}(\text{C}_6\text{H}_4\text{OH})_2$. With acid catalysts acetaldehyde and three moles or less of phenol yield soluble resins. Hardenable resins are difficult to produce by the alkaline condensation of acetaldehyde and phenol as acetaldehyde tends to undergo aldol condensation and self-resinification.

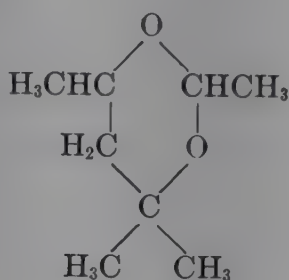
Reactions with Halogens and Halogen Compounds. Halogens readily replace the hydrogen atoms of the methyl group—for example, chlorine reacts with acetaldehyde or paraldehyde at room temperature to give chloroacetaldehyde, ClCH_2CHO ; increasing the temperature to 70–80°C gives dichloroacetaldehyde, Cl_2CHCHO ; and at a temperature of 80–90°C chloral, Cl_3CCHO , is formed (93). The catalytic chlorination with an antimony powder or aluminum chloride–ferric chloride has been described (94). Bromal, Br_3CCHO , is formed by an analogous series of reactions (95). It has been postulated that acetyl bromide, CH_3COBr , is an intermediate in the bromination of acetaldehyde in aqueous ethanol (96). Acetyl chloride, CH_3COCl , has been prepared by the gas phase reaction of acetaldehyde and chlorine (97).

The oxygen atom in acetaldehyde can be replaced by reacting the aldehyde with phosphorus pentachloride to produce 1,1-dichloroethane, CH_3CHCl_2 . Hypochlorite and hypiodite react with acetaldehyde yielding chloroform, CHCl_3 , and iodoform, CHI_3 , respectively. Phosgene, COCl_2 , is produced by the reaction of carbon tetrachloride with acetaldehyde in the presence of anhydrous aluminum chloride (98). Chloroform reacts with acetaldehyde in the presence of potassium hydroxide and sodium amide to form 1,1,1-trichloro-2-propanol, $\text{CH}_3\text{CH}(\text{OH})\text{CCl}_3$ (99).

Miscellaneous Reactions. Sodium bisulfite, NaHSO_3 , adds to acetaldehyde to form a white crystalline addition compound, insoluble in ethyl alcohol and ether. The bisulfite addition compound frequently is used to isolate acetaldehyde from solution and for purification; the aldehyde is regenerated with dilute acid. Hydrocyanic acid adds to acetaldehyde in the presence of an alkali catalyst to form the cyanohydrin, $\text{CH}_3\text{CH}(\text{OH})\text{CN}$; the cyanohydrin may also be prepared by reacting sodium cyanide with the bisulfite addition compound. Acrylonitrile (qv), $\text{CH}_2=\text{CHCN}$, is made commercially by reacting acetaldehyde with hydrocyanic acid and heating the cyanohydrin to 600–700°C (100). Alanine, $\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$, can be prepared by reacting an ammonium salt and an alkali metal cyanide with acetaldehyde; this is the Strecker amino acid synthesis, a general method for the preparation of α -amino acids. Grignard reagents add readily to acetaldehyde, the final product being a secondary alcohol. Thioacetaldehyde, CH_3CHS , is formed by reaction of acetaldehyde with hydrogen sulfide; thioacetaldehyde polymerizes readily to the trimer.

Acetic anhydride adds to acetaldehyde forming ethylidene diacetate, $\text{CH}_3\text{CH}(\text{OOCCH}_3)_2$, in the presence of dilute acid; boron fluoride is also a catalyst for the reaction (101). Ethylidene diacetate is decomposed to the anhydride and aldehyde at temperatures of 220–268°C and initial pressures of 11 to 46 cm Hg (102), or by heating to 150°C with a zinc chloride catalyst (103). Acetone has been prepared in 90%

yield by heating an aqueous solution of acetaldehyde to 410°C in the presence of a catalyst (104). Acetaldehyde can be condensed with active methylene groups: with nitromethane, CH_3NO_2 , products are $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{NO}_2$ or $(\text{CH}_3\text{CH}(\text{OH}))_2\text{CHNO}_2$ (105); with ethyl-3-bromopropionate, $\text{CH}_2\text{BrCH}_2\text{COOC}_2\text{H}_5$, and a magnesium-mercuric chloride catalyst, 2-pentenoic acid, $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCOOH}$, is formed (106); with diethyl malonate, $\text{CH}_2(\text{COOC}_2\text{H}_5)_2$, the stable diethyl (1-hydroxyethyl)malonate, $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{COOC}_2\text{H}_5)_2$ is the product (107). Ethanol, 1-butanol, and 2-methyl-1-pentanol have been prepared by reacting acetaldehyde, carbon monoxide, and hydrogen at 120–200°C and 2000 psi in the presence of a cobalt carbonyl (108). High-molecular-weight ketones have been made by the reaction of acetaldehyde with ethylene and oxygen at 55°C and 3000 psi (109). The reaction of isobutylene with aqueous solutions of acetaldehyde in the presence of 1–2% sulfuric acid yields alkyl-*m*-dioxanes, the principal product being 2,4,4,6-tetramethyl-*m*-dioxane in yields up to 90% (110).



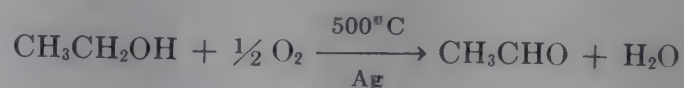
Manufacture

Acetaldehyde is produced commercially by (1) the vapor phase dehydrogenation or partial oxidation of ethyl alcohol, (2) the liquid phase hydration of acetylene, (3) high-temperature oxidation of saturated hydrocarbons, or (4) the liquid phase oxidation of ethylene. The ethylene oxidation process may become the principal route to acetaldehyde in the future.

FROM ETHYL ALCOHOL

Acetaldehyde may be produced from ethyl alcohol either by catalytic oxidation or dehydrogenation, the former being the most important industrially.

The ethyl alcohol oxidation is carried out by passing alcohol vapors and preheated air over a catalyst, preferably silver, at 300–575°C (111),



The reactor temperature depends on the air-ethyl alcohol-steam ratio and the velocity of the gases over the catalyst. Alcohol conversion per pass generally varies from 25 to 35% and yields are 85 to 95%. The unreacted alcohol and acetaldehyde are scrubbed from the exit gas with cold dilute alcohol. The acetaldehyde and ethyl alcohol are separated by distillation and the dilute alcohol from the still is concentrated and recycled. Acetic acid, formic acid, ethyl acetate, methane, and carbon monoxide are formed as by-products. Copper oxidation catalysts have also been used; Saito has investigated the oxidation and dehydrogenation of alcohol over ten metal oxide catalysts (112). Violent oxidation occurred with the oxides of manganese, cobalt, nickel, vanadium, and iron.

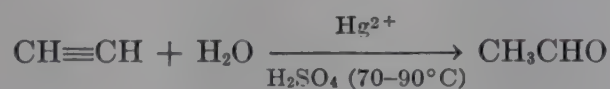
Acetaldehyde has been prepared by dehydrogenation of ethyl alcohol for more than thirty years. Ethanol is vaporized and passed over a chromium-activated copper catalyst at essentially atmospheric pressure and 260–290°C (111).



The conversion of alcohol to aldehyde per pass generally is 30 to 50%: it is controlled by the rate of flow of the alcohol over the catalyst and the reaction temperature. The yield of acetaldehyde is over 90%. Small amounts of acetic acid, ethyl acetate, and 1-butanol are formed as by-products. The products are condensed and the gases are scrubbed to recover alcohol and acetaldehyde which are separated by distillation of the aqueous solution. The unreacted alcohol is recycled to the process. The catalyst requires periodic reactivation but has a normal life of several years. The by-product hydrogen which contains small concentrations of methane and carbon dioxide, is suitable for hydrogenation. Church and Joshi have reported conversion as high as 95% and yields of 88% acetaldehyde from the dehydrogenation of alcohol over a supported copper catalyst containing 5% cobalt and 2% chromium as promoters at 275–300°C; a 10% yield of ethyl acetate was also obtained (113). Conversion and acetaldehyde yields of 72 and 98%, respectively, have been reported for the dehydrogenation of alcohol over a supported copper oxide–chromium oxide–alkali metal salt catalyst (114).

FROM ACETYLENE

Acetaldehyde has been produced commercially by the hydration of acetylene for approximately fifty years. In the older processes, acetylene of high purity is passed under a pressure of 15 psi into a vertical reactor containing a mercury catalyst dissolved in 18 to 25% sulfuric acid; the reaction temperature is maintained at 70–100°C:



Fresh catalyst is fed to the reactor periodically; the catalyst may be added in the mercurous form but it has been shown that the catalytic species is a mercuric ion complex (115). The excess acetylene sweeps out the dissolved acetaldehyde which is condensed by water and refrigerated brine and scrubbed with water; the crude acetaldehyde is purified by distillation and the unreacted acetylene is recycled. The catalytic mercuric ion is reduced to catalytically inactive mercurous sulfate and metallic mercury; this sludge, consisting of reduced catalyst and tars, is drained from the reactor at intervals and resulfated. The rate of catalyst depletion can be reduced by adding ferric or other salts to the reaction solution. The ferric ion reoxidizes mercurous to the mercuric ion while it is reduced to the ferrous state; consequently, the quantity of sludge which must be recovered is reduced. The revised mercuric–iron salt catalyst system has been widely used in recent years (103,116). In another variation acetylene is completely hydrated with water in a single operation at 68–73°C using the mercuric–iron salt catalyst. The acetaldehyde is partially removed by vacuum distillation and the mother liquor recycled to the reactor. The aldehyde vapors are cooled to about 35°C, compressed to 2.5 atm, and condensed. It is claimed that this combination of vacuum and pressure operations substantially reduces heating and refrigeration costs

(117). For the conventional reaction system, 50–60% of the acetylene is converted per pass and acetaldehyde yields are greater than 95%. The principal by-products formed are acetic acid and crotonaldehyde.

The vapor phase hydration of acetylene over solid catalysts has been studied intensively; catalysts containing phosphate salts have been found to be particularly effective (118,119). It is unlikely that vapor phase hydration will be developed commercially.

Acetaldehyde may also be made from methyl vinyl ether and ethylidene diacetate, both of which can be made from acetylene. Methyl vinyl ether, $\text{CH}_3\text{OCH}=\text{CH}_2$, is made by the addition of methanol to acetylene at 16 atm pressure in a vertical reactor containing a 20% solution of potassium hydroxide in methanol. Hydrolysis of the ether with dilute sulfuric acid yields acetaldehyde and methanol which are separated by distillation; the methanol is recycled to the reactor. Acetylene and acetic acid form ethylidene diacetate in the presence of mercuric oxide and sulfuric acid at 60–80°C and atmospheric pressure. After separation the ethylidene diacetate is decomposed to acetaldehyde and acetic anhydride by heating to 150°C with a zinc chloride catalyst (103). Acetaldehyde has been made both from methyl vinyl ether and ethylidene diacetate in the past, but neither process is used today.

FROM SATURATED HYDROCARBONS

Acetaldehyde is made commercially by the vapor phase oxidation of saturated hydrocarbons, such as butane or mixtures containing butane, with air or oxygen. In one variation, the hydrocarbon stream is mixed with compressed air and recycle gas, which contains unreacted hydrocarbons, carbon monoxide, carbon dioxide, and nitrogen; preheated at 100 psig to 370°C; and oxidized at 450°C. After decomposition of peroxides over a ceramic catalyst packed in the outlet of the reactor coil, the hot gases are quenched by scrubbing with cold dilute aqueous formaldehyde solution. The product stream is scrubbed with water to recover oxygenated compounds and the unreacted hydrocarbons and fixed gases are vented and recycled or recovered. The oxygenated products are separated from water by flashing and the pure compounds are isolated by a complex purification procedure utilizing fractional, azeotropic, and extractive distillations as well as extraction. Oxidation of *n*-butane yields acetaldehyde, formaldehyde, methanol, acetone, and mixed solvents as major products; other aldehydes, alcohols, ketones, glycols, acetals, epoxides, and organic acids are formed in smaller concentrations. The composition of the product mixture depends to some extent on the hydrocarbon taken as starting material. The highest yield of acetaldehyde is obtained by oxidation of *n*-butane and by oxidizing with oxygen rather than air (120). (See also Hydrocarbon oxidation.)

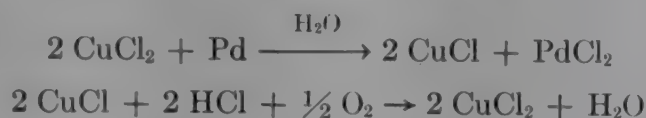
OXIDATION OF ETHYLENE

The direct liquid-phase oxidation of ethylene, a process developed by Consortium für Electrochemische G.m.b.H., a subsidiary of Wacker Chemie G.m.b.H., is the most recent method developed for the manufacture of acetaldehyde. Either air or oxygen can be used in the catalytic oxidation of ethylene; the oxygen and air variants of the process have been developed by Farbwerke Hoechst G.m.b.H. and Wacker Chemie G.m.b.H. Both processes are licensed by a joint company, Aldehyd G.m.b.H. In the preferred method, ethylene is oxidized to acetaldehyde in a dilute hydrochloric

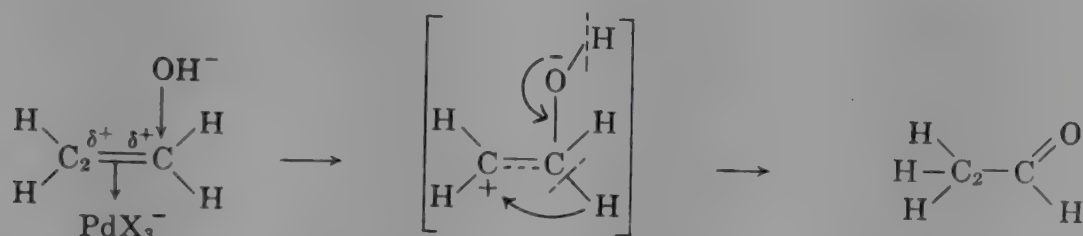
acid solution containing the chlorides of palladium and copper at moderate temperatures and pressures. Ethylene stoichiometrically forms a complex with palladium chloride; on hydrolysis this complex yields acetaldehyde and palladium metal,



For a continuous reaction the inactive palladium metal must be reoxidized to palladium chloride; it has been found that cupric chloride is the most suitable oxidizing agent as it readily reoxidizes the palladium metal and the cuprous chloride formed in this reaction can be reoxidized to the cupric salt with oxygen or air.



The net result is a one-step process in which ethylene is oxidized continuously to acetaldehyde through a complex series of oxidation-reduction reactions (121). It has been demonstrated that the ethylene-palladium salt complex is hydrolyzed by attack of a hydroxide ion on the complex-bound olefin followed by the transfer of the π electron pair of the olefin to palladium, the migration of a hydride ion from carbon 1 to carbon 2, the formation of a double bond between carbon 1 and oxygen, and the removal of a proton (122).



It will be noted that oxygen participates only indirectly in the oxidation of ethylene.

There are two variations for the production of acetaldehyde by oxidation of ethylene, the one-stage and two-stage processes (123,124). In the *one-stage process* (Fig. 1) all the oxidation-reduction reactions involved in the oxidation of ethylene take place simultaneously in a vertical reactor at an elevated temperature and under a slight pressure. In the *two-stage process*, the ethylene is oxidized in one reactor at temperatures and pressures somewhat higher than in the one-stage process. The spent catalyst is pumped to a separate regenerator where it is reoxidized with air, and then recycled to the ethylene converter. Acetaldehyde is recovered from either process by scrubbing with water and is purified by distillation. The tail gas from the scrubber is split; a small amount is bled from the system while the remainder is recycled to the ethylene reactor. The yields of acetaldehyde are approximately 95%. The crude acetaldehyde contains small amounts of by-products, chiefly chlorinated organic compounds and organic acids.

This oxidation of olefins has been exploited commercially to date only for the production of acetaldehyde, but the reaction can be applied to most olefinic compounds, the products being primarily ketones (121,122). Vinyl acetate has been made in the laboratory by a variation of this reaction (32). The catalytic oxidation of ethylene to acetaldehyde with chloroauric acid which is reduced to metallic gold has been reported; simultaneously or subsequently the metal is reconverted to chloroauric acid by oxidation with nitric oxide or a higher oxide of nitrogen (125). The preparation of acetaldehyde by the oxidation of ethylene in a sulfuric acid solution containing the

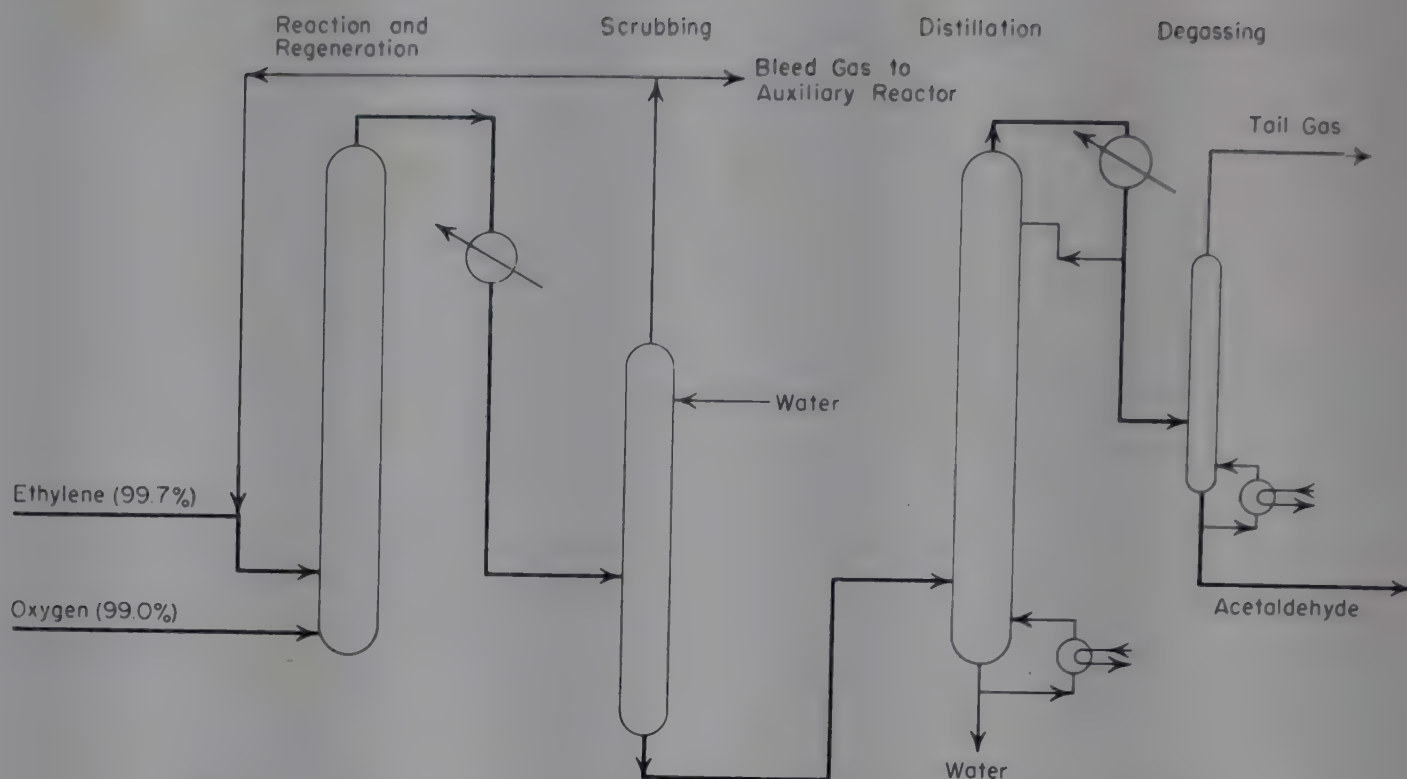


Fig. 1. Acetaldehyde from ethylene by single-stage oxidation with oxygen.

catalyst vanadium pentoxide at relatively high temperatures and pressures has been described; the reduced vanadium is reoxidized to the pentavalent state with oxygen (126).

Economic Aspects

The production pattern for acetaldehyde has changed significantly since 1940. At that time the principal industrial routes to acetaldehyde were hydration of acetylene and oxidation of ethyl alcohol. However, increasing acetylene costs have made the hydration process less attractive economically. At the present time, no acetaldehyde is manufactured in the United States from acetylene. The source materials for acetaldehyde made in the United States in recent years have been ethanol and, to a lesser extent, saturated hydrocarbons. In 1960 the two Aldehyd G.m.b.H. processes for the liquid phase oxidation of ethylene to acetaldehyde began commercial operation; as high yields of acetaldehyde are obtained from the comparatively inexpensive petrochemical, ethylene, these processes offered to many producers a cheaper process for acetaldehyde manufacture. In the two years since the first plants for the production of acetaldehyde from ethylene began operation, at least thirteen major companies have licensed the Aldehyd G.m.b.H. processes. Included among the licensees are companies that presently produce acetaldehyde from ethanol and by oxidation of saturated hydrocarbons as well as companies that have based their operations on acetylene hydration. The rapid acceptance by industry of the ethylene oxidation processes has been remarkable, and the one-step oxidation of ethylene may become the standard process for acetaldehyde manufacture in future years.

Accurate production data are difficult to obtain as the bulk of the acetaldehyde produced is used internally by the manufacturer. Moreover, most of the products that are made from acetaldehyde are also produced from other starting materials, further complicating the problem. No data are available for world production. However, Hester and Himmler have published data for the production of some chem-

icals derived from acetaldehyde—acetone, acetic acid, butyl acetate, ethyl acetate, methyl acetate, and 1-butanol (127). Although several important products made from acetaldehyde are not included in this list, and it is unlikely that all the products listed were derived exclusively from acetaldehyde, the data of Hester and Himmler can be used to make a rough estimate of acetaldehyde production in some of the western countries. The following figures for acetaldehyde production in West Germany, France, Italy, Great Britain, Japan, and the United States are based on the assumption that the products tabulated by Hester and Himmler were derived exclusively from acetaldehyde.

<i>Year</i>	<i>Acetaldehyde produced, million lb</i>
1952	1330
1954	1730
1956	2140
1957	2200

Complete production figures are not readily available even for the United States. The best estimate of acetaldehyde production is provided by the data published for the volume of ethyl alcohol converted to aldehyde (128) (see Table 5). While figures derived solely from this source will be low to the extent that acetaldehyde has been produced from other starting materials, notably paraffin oxidation, they do indicate the pattern of acetaldehyde production over the past twenty years. The oxidation of

Table 5. Acetaldehyde Produced from Ethanol

<i>Year</i>	<i>Acetaldehyde, million lb</i>	<i>Year</i>	<i>Acetaldehyde, million lb</i>	<i>Year</i>	<i>Acetaldehyde, million lb</i>
1940	140	1947	370	1954	560
1941	170	1948	420	1955	660
1942	196	1949	500	1956	700
1943	254	1950	500	1957	700
1944	340	1951	630	1958	720
1945	320	1952	590	1959	790
1946	310	1953	640	1960	900

saturated hydrocarbons has become an increasingly important source of acetaldehyde; hence, production figures for aldehyde based solely on ethyl alcohol usage will be most in error for the period 1955–1960. It has been estimated that there is sufficient paraffin oxidation plant capacity to supply approximately 30% of the total possible acetaldehyde production in 1962 (129). In Table 5, an acetaldehyde yield of 95% from 95% alcohol has been assumed; no attempt has been made to correct for acetaldehyde from other sources.

The price of acetaldehyde has decreased since 1936 from 14 to 10¢ per pound in 1962 for tank car lots. Over the last ten years the price has varied between 9.5 and 10.5¢ per pound in bulk quantities. However, the quoted price of acetaldehyde is not too meaningful as only approximately 5% of the total production is sold, the remainder being used in captive processes.

Acetaldehyde production is linked with the demand for cellulose acetate, vinyl acetate resins, acetate esters, 1-butanol, 2-ethylhexanol, chloroacetic acid, chloral, pentaerythritol, synthetic pyridine derivatives, and the like. Many of the products

derived from acetaldehyde compete directly for markets which can be satisfied with materials made from other starting materials. Consequently, price is the determining factor in many instances; hence, growth of acetaldehyde and aldehyde-derived chemicals is dependent primarily on reduced aldehyde production costs.

Specifications, Analytical and Test Methods

Commercial acetaldehyde has the following typical specifications: assay 99% minimum; color water-white; acidity 0.5% maximum (as acetic); specific gravity 0.790 at 20°C; boiling point 20.8°C at 760 mm Hg. Acetaldehyde is shipped in steel drums and tank cars bearing the ICC red label. In the liquid state it is noncorrosive to most metals; however, it oxidizes readily, particularly in the vapor state, to acetic acid. Precautions to be observed in the handling of acetaldehyde have been published by the Manufacturing Chemists Association (130).

Analytical methods based on many of the reactions common to aldehydes have been developed for the determination of acetaldehyde. In the absence of other aldehydes it can be detected by the formation of a mirror from an alkaline silver nitrate solution (Tollens' reagent) and by the reduction of Fehling's solution. It can be determined quantitatively by fuchsin-sulfite solution (Schiff's reagent) or by the reaction with sodium bisulfite, the excess bisulfite being estimated iodometrically. Acetaldehyde present in mixtures with other carbonyl compounds, organic acids, etc, can be determined by paper chromatography of 2,4-dinitrophenylhydrazones (131), by polarographic analysis either of the untreated mixture (132), or of the semicarbazones (133), the color reaction with thymol blue on silica gel (detector tube method) (134), mercurimetric oxidation (135), argentometric titration (136), microscopic (137) and spectrophotometric methods (138), and gas-liquid chromatographic analysis (139). With the advent of gas-liquid chromatographic techniques, this method has superseded most chemical tests for routine analyses. In the Shawinigan Chemicals Limited laboratory, columns of 3,3'-oxydipropionitrile on Chromosorb W have been found to be particularly effective for the gas-chromatographic separation of acetaldehyde from low-boiling carbonyl compounds, epoxides, and organic acids at temperatures below 90°C.

Acetaldehyde can be isolated and identified by the crystalline compounds of characteristic melting points formed with hydrazines, semicarbazides, etc; these derivatives of aldehydes can be separated by paper and column chromatography (131, 140). Acetaldehyde has been separated quantitatively from other carbonyl compounds on an ion exchange resin in the bisulfite form; the aldehyde is eluted from the column with a solution of sodium chloride (141). In larger quantities it may be isolated by passing the vapor into ether and saturating the ether with dry ammonia; the product, acetaldehyde-ammonia, crystallizes from the ether solution. The reactions of acetaldehyde with bisulfite, hydrazines, oximes, semicarbazones, and 5,5-dimethyl-1,3-cyclohexanedione (Dimedon) also have been used to isolate acetaldehyde from solutions.

Health and Safety Factors

Physiological Effects. Acetaldehyde has a general narcotic action on the nervous system. It causes irritation of the eyes and mucous membranes, and accelerates the action of the heart. When breathed in high concentrations, it causes headaches and

has a temporary suffocating effect on the lungs. Prolonged exposure causes a decrease of both white and red cells and hemoglobin; there is also a sustained rise in blood pressure (142–144). The maximum allowable concentration of acetaldehyde in air is 200 ppm (145). In normal industrial operations there is no health hazard in handling acetaldehyde provided elementary precautions are taken.

Industrial Hazards. Mixtures of acetaldehyde vapor with air are flammable and explosive if the concentrations of aldehyde and oxygen rise above 4 and 9%, respectively. See under Physical properties, p. 78, and reference 130 for handling precautions.

Uses

Approximately 95% of the acetaldehyde produced is used internally by the manufacturers as an intermediate leading to other organic chemicals. It is difficult to estimate the exact distribution of acetaldehyde consumption as many of the major products derived from aldehyde are also made from other starting materials. A 1954 estimate showed the following end-use pattern, in percent consumption, for American producers (146):

acetic acid	47
<i>n</i> -butyl alcohol	29
acetic anhydride	12
2-ethylhexanol and other aldol products	7
pentaerythritol	3.6
pyridines, chloral, etc	1.4

Acetic acid is without question the largest single product manufactured from acetaldehyde. The three main uses for acetic acid are in the production of vinyl acetate, monochloroacetic acid, and acetate esters. The market for vinyl acetate has the greatest influence on acetic acid and, consequently, on acetaldehyde production. Acetic anhydride, which is used to make cellulose acetate, is related closely to the fortunes of the textile industry. The third acid which can be derived from acetaldehyde, peroxyacetic acid, is made only in relatively small quantities at the present time; to date it is used primarily in the manufacture of epoxides, but it does have potential in other areas such as bleaching. It is expected that peroxyacetic acid will assume greater importance in the immediate future.

Products made by the aldol condensation sequence of reactions have become important outlets for acetaldehyde. The two major products derived from acetaldehyde via the aldol route are 1-butanol (see Butyl alcohols) and 2-ethylhexanol (see Alcohols, higher, synthetic). The butanol is used mainly as butyl acetate, a solvent for nitrocellulose lacquers. At one time butyl acetate was the most important lacquer solvent in the medium-boiling range, but in recent years there has been increasing competition from other solvents and little growth is expected in the future. On the other hand, the consumption of 2-ethylhexanol has almost doubled in the last five years; it is used to make "dioctyl" phthalate, the largest volume plasticizer for polyvinyl chloride resins. 2-Ethylhexanol has received increasing competition from the oxo alcohols, but lower acetaldehyde costs should permit it to retain its position in this field. Other products which are produced in small quantities from the aldol sequence of reactions are 1,3-butylene glycol (1,3-butanediol), crotonic acid, and butyric acid.

Pentaerythritol (see Alcohols, polyhydric), which is made by the condensation of acetaldehyde with formaldehyde, is the next largest consumer of aldehyde. As the principal end use for pentaerythritol is in the alkyd resin field, it competes directly with glycerol; hence future expansion in this area depends to a large extent on the relative costs of the two polyols.

Chloral, synthetic pyridines, and ethyl acetate require a considerable volume of acetaldehyde. DDT, which is made from chloral, has become a large-volume item since 1944. The production of synthetic pyridines made from paraldehyde and ammonia is of growing importance; 5-ethyl-2-methylpyridine is an intermediate in the manufacture of 2-methyl-5-vinylpyridine, nicotinic acid, and pharmaceuticals. Ethyl acetate has been made for a number of years in Canada and Germany directly from acetaldehyde by the Tishchenko condensation; ethyl acetate has lost its former pre-eminent position in the solvent field and little future growth is expected. Acrylonitrile is made commercially in Germany from acetaldehyde cyanohydrin derived from the reaction of acetaldehyde and hydrocyanic acid. As the manufacture of acrylonitrile from propylene, ammonia, and oxygen offers distinct economic advantages, it is not expected that the aldehyde route to acrylonitrile will be competitive. (See Acrylonitrile.)

Acetaldehyde has a number of minor industrial uses: the condensation products with phenol or urea are thermosetting resins; the reaction with aliphatic and aromatic amines gives Schiff bases which are used as accelerators and antioxidants in the rubber industry; polyvinyl acetal resins are produced in small quantities; mirrors have been silver-coated by the reduction of ammoniacal silver nitrate to silver. Acetaldehyde has been used as a denaturant for ethyl alcohol, as a preservative for fruit and fish, in fuel compositions, for hardening gelatin, glue, and casein products, and for the prevention of mold growth on leather; current consumption for these purposes, however, is very small. Butadiene has been made by the reaction of ethyl alcohol and acetaldehyde in times of rubber shortage.

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ACETAL RESINS

The generic term "acetal resin" has been accepted to describe those thermoplastics produced by the addition polymerization of aldehydes through the carbonyl function. It is the generic term covering Delrin, the trade name for a new engineering material announced and introduced in 1957 by E. I. du Pont de Nemours & Co., Inc.

The raw material for Delrin is formaldehyde (qv). Because formaldehyde is one of the most abundant and lowest cost organic raw materials, and because the acetal resins derived from it possess a remarkably useful combination of properties, it is forecast that the market for them will grow rapidly. Acetal resins are being used as replacements for metals, both ferrous and nonferrous, glass, wood, rubber, and, to some extent, other plastics.

The generic term acetal resin also covers Celcon (Celanese Corporation of America), a copolymer formed from trioxane (the cyclic trimer of formaldehyde). Celcon was announced and introduced in 1961.

A polymer of formaldehyde was first obtained more or less inadvertently over one-hundred years ago by the Russian chemist, Butlerov (1). However, the polymer he observed, as well as the typical low-weight polymers of today, including paraformaldehyde and similar species, are solids that melt with rapid decomposition at about 150°C. They range in molecular weight up to about 3000, but possess none of the mechanical properties of the acetal resins.

The chemical structure of formaldehyde polymers, though first correctly proposed by Delépine in 1897, was challenged later by Auerbach and Barshall. Thus, the true structure remained obscure until confirmed by the thorough investigations of Hermann Staudinger and his collaborators during the 1920s (2).

In the course of the past 20 years, work carried on by the Du Pont Company has led to the discovery of ways to polymerize formaldehyde to high-molecular-weight polymers having high thermal stability. Thus, for the first time, it became possible to assess and to utilize fully the unusual combination of chemical and physical properties which, today, places the acetal resins in an important commercial position.

Work of the Staudinger school established that formaldehyde forms long, thread-like polymer molecules when it is polymerized. Because these products were shown to be composed of repeating oxymethylene units, $\text{—OCH}_2\text{—}$, they were called "polyoxymethylenes." As derived, such polymers usually possess mostly hydroxyl end groups so that they can be represented as $\text{H(OCH}_2)_n\text{OH}$, and are therefore often referred to as "polyoxymethylene glycols" in the early literature. However, in keeping with more modern conventions of polymer nomenclature, and in recognition of the fact that polymerization occurs by addition across the carbonyl double bond, one may quite properly refer to them as "polyformaldehydes." Recently the generic term, acetal resin, has been accepted to describe these polymers since their typically alternating carbon-oxygen chain structure imparts to them the chemistry commonly ascribed to the simple acetals of classical organic chemistry. When acetal resins are derived from formaldehyde, the repeating unit is oxymethylene. If they are derived from higher aldehydes, the repeat unit is a substituted oxymethylene, —OCRH— .

Depending upon the system in which polymerization takes place, the terminal groups of the polymer chains may be hydroxyl or partly alkyl or acyl, or the hydroxyl end groups may be replaced through chemical reaction by these functions. However, the nature of the end groups is not particularly important to the intrinsic mechanical properties of acetal resins, although the thermal and chemical stabilities are affected by them. The mechanical properties of the acetal resins result from the ability of the oxymethylene chains to pack together into a highly ordered, crystalline configuration as the polymers change from the molten to the solid state. This occurs regardless of the particular nature of the end groups.

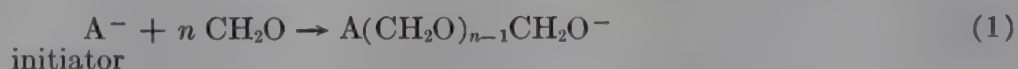
Polymerization

Polymerization of Formaldehyde. A review of the early work on the polymerization of formaldehyde as well as later studies carried out by Du Pont and others serves to emphasize the importance of ionic initiation. It is not often that one finds a monomer that can be polymerized so readily by either cationic or anionic initiators: common acids and bases, organic acids, Lewis acids, amines, aluminum and other metal oxides, organometallic compounds, quaternary ammonium or phosphonium compounds, phosphines, arsines, stibines, metal carbonyls, carbodiimides ($\text{RN}=\text{C}=\text{NR}$), *N*-methylolethers ($\text{RCONHCH}_2\text{OR}'$) or thioethers, azomethines, elemental sulfur, and triamides of boron. Ionizing radiation also brings about polymerization (3). The monomer is readily polymerized either in bulk, from a nonreactive medium, or directly as a vapor.

From the foregoing, it would appear that the polymerization of formaldehyde is indeed facile. However, impurities in the polymerization system have a profound effect upon the molecular weight and the stability of the polymer produced. Thus in any practical scheme for converting formaldehyde to a useful high polymer, monomer of high purity must be employed.

During polymerization, any impurity capable of undergoing an ionic reaction may influence the molecular weight of the product. This is because the polymer molecule continues to grow until it reacts with an impurity capable of chain transfer. During transfer, a new ion is produced which in turn acts as an initiator to start a new polymer chain. Thus, in a typical polymerization, relatively few of the polymer molecules are initiated by the added initiator. Most of the polymer molecules are initiated by chain transfer.

Initiation and subsequent chain transfer with a water molecule during polymerization may be depicted simply as follows:



In step 1 polymerization has been initiated by nucleophilic attack on formaldehyde followed by addition of formaldehyde units to produce an oxymethylene chain. In step 2 the growing chain interacts with water to complete the growth of the molecular chain and liberate a hydroxyl ion. Step 3 depicts initiation of a new chain by the hydroxyl ion and subsequent chain growth.

Schemes by which formaldehyde can be purified most effectively are to be found in the patent literature (4). These include scrubbing with an inert liquid, partial polymerization to remove chain-transfer impurities, conversion of formaldehyde to a hemiformal and subsequent thermal decomposition to purified formaldehyde, and dehydration by contacting with P_2O_5 .

The process by which Du Pont manufactures Delrin acetal resin has not been made public. However, a typical polymerization of formaldehyde as described in the patent literature (3b) is as follows: Formaldehyde monomer is prepared by the pyrolysis at 150–160°C of alkali-precipitated formaldehyde low polymer which has been carefully washed and dried. The monomeric formaldehyde that is evolved is, if desired, further purified by passage through several cold traps at -15°C . The substantially

anhydrous formaldehyde gas is introduced into the polymerization vessel above the surface of a rapidly agitated, inert liquid medium containing the initiator. The medium, heptane, for example, is carefully dried. If triphenylphosphine is used as the initiator, it is added to the extent of about 20 ppm based on the medium. Diphenylamine, which helps to stabilize the polymer after isolation, may be added at a concentration of about 100 ppm. Polymerization is continued until the medium contains about 20% solids. The flow of monomer is terminated and the polymer is isolated by filtration. The raw polymer is washed with fresh heptane and then with acetone and is dried.

Polymerization of Trioxane. An alternate method by which acetal resin may be derived is the polymerization of trioxane, perhaps the simplest polymer of formaldehyde. Trioxane may be induced to undergo further polymerization to a high polymer upon contact with cationic initiators either in bulk or dissolved in an inert medium, such as cyclohexane (5). The polymers thus obtained possess structures and properties similar to those derived directly from formaldehyde. Unlike formaldehyde, anionic initiators do not yield high polymers from trioxane.

Stabilization of Acetal Resins. Once a high molecular weight has been achieved, a formaldehyde polymer will possess mechanical properties that are fully developed. However, if the molecular chains of a given polymer are terminated by hydroxyl groups, this polymer will be less stable and therefore less generally useful than one wherein the chain ends are terminated by alkyl or acyl groups (6). It is advantageous, therefore, to react the raw polymer with some reagent that will bring about the desired conversion of the end groups. Conveniently, this may be acetic anhydride, thus leading to a diacetate type of acetal resin.

Esterification of the raw polymer may be carried out as described in the patent literature (6a). Typically, the raw polymer, carefully dried, is mixed with about 10 volumes of purified acetic anhydride containing 0.1% by weight of sodium acetate catalyst. The mixture is stirred and heated to reflux for about 30 minutes. After cooling, the granular product is recovered by filtration and washed thoroughly with water and then acetone. An antioxidant or other thermal stabilizer is then added.

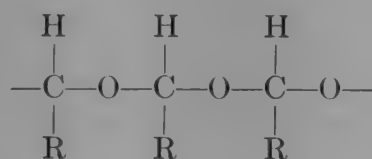
As is typical of other resins and plastics in general, further stabilization is also imparted to acetal resins by the incorporation of antioxidants and other stabilizers, notably amides and amines. The various modes of degradation of polyoxymethylenes have been studied in detail by Kern and Cherdron (7). Chief among these are unraveling from free hydroxyl ends and random attack on the polymer chain by oxygen and/or acids. Although the patent literature on stabilizers is not yet as extensive as that on polymerization, it, too, is growing rapidly (8).

Copolymerization of Formaldehyde. Compared to homopolymerization of formaldehyde, little has been published on copolymerization. One patent has been issued on the copolymers of formaldehyde and perfluoroaldehydes—for example, trifluoroacetaldehyde (9). These acetal copolymers are not yet of commercial interest.

Copolymerization of Trioxane. Acetal copolymers of commercial interest are derived by a cationically initiated copolymerization employing trioxane in place of formaldehyde, together with a second monomer. Comonomers frequently employed belong to the class of oxacyclic compounds having at least one C—C bond in the ring. Examples are the olefin oxides, such as ethylene or propylene oxide, or cyclic formals, such as 1,3-dioxane (10). In addition to these, however, Kern (11) reports that trioxane may be copolymerized readily with various unsaturated compounds that are cationically polymerizable. Included here are styrene, vinyl ethers, vinyl acetate,

methyl vinyl ketone, and others. These copolymerizations may be carried out in bulk or in an inert medium, such as cyclohexane. Highest molecular weights are generally obtained from the most carefully purified systems. The dominant structural feature of all these many copolymers, however, is a molecular chain of alternating carbon and oxygen atoms; these chains are interrupted infrequently by C—C bonds derived from the comonomer. It is the presence of alternating oxygen-carbon chain segments that imparts to these copolymers the properties of acetal resins and thus permits of their classification as such.

Polymerization of Higher Aldehydes. As might be expected, acetal resins of the following type have been obtained from a variety of higher aldehydes:



Polymerization occurs through the carbon-oxygen double bond in each case. However, the addition of each new monomer unit produces an asymmetric center and consequently polymers with stereoregularity may result. Although the study of high polymers of these higher aldehydes dates back to the late twenties and early thirties, it has been only recently that well-defined atactic and isotactic forms have been synthesized and characterized. In spite of this renewed interest, none of these higher aldehyde polymers has achieved commercial interest.

Some 30 years ago, work by Conant and his co-workers (12) showed that several of the higher aldehydes, notably *n*- and isobutyraldehydes, could be converted to soft, waxy solids or hard amorphous masses when subjected to pressures of 12,000 atmospheres. *n*-Valeraldehyde and *n*-heptaldehyde were similarly polymerized to thick pastes. In the light of recent work, these polymers appear to be the atactic modifications. The alternating —C—O—C— backbone structure, typical of today's acetal resins, was proposed for them, and their marked tendency to depolymerize spontaneously was noted. More recently these polymers were again prepared under high pressure by Novak and Whalley (13) and the infrared spectra and structures were characterized. This work confirmed the structures proposed earlier.

Polymers of acetaldehyde were first prepared independently by Letort (14) and by Travers (15) when the aldehyde was crystallized at -123°C and then allowed to melt. The product is a rubbery solid and is now known to be the noncrystalline, atactic form. This same atactic form may also be obtained, as reported by Vogl (16), when acetaldehyde is polymerized in an inert solvent, such as toluene, or in liquid propylene at a temperature below -40°C using either a Lewis acid or a protonic acid as the initiator.

Crystalline polyacetaldehyde, the isotactic form of the polymer, which is a plastic rather than an elastomer, was first reported by Vogl (17). It is perhaps worth noting that its preparation constituted the first known example of a stereoselective polymerization involving double bonds other than carbon-carbon double bonds. The isotactic polymer is obtained by an anionic polymerization of acetaldehyde. Polymerization is carried out in an inert medium, such as toluene, propylene, or isobutylene, at temperatures below about -40°C . Initiators such as alkali alkoxides (lithium *sec*-butoxide), lithium aluminum hydride (LiAlH_4), and alkali metal alkyls (butyllithium) are effective. The crystalline form of polyacetaldehyde melts at

about 165°C and, unlike the amorphous elastomer, is practically insoluble at room temperature in many common solvents. Crystalline polymers of other higher aldehydes were prepared in a similar manner.

In 1960, several publications appeared which showed that independent research on isotactic polymers of the higher aldehydes was being actively pursued. In addition to a publication by Vogl (16), Furukawa (18) and Natta (19) each published extensively on the subject. Low-temperature, ionic polymerization was reported to give highly crystalline products from the common aldehydes up through C₇. Preferred catalysts included numerous organometallic compounds, such as diethylzinc and triethylaluminum. The stereorelationships of these new polymers were described in detail by Natta. Mechanical and general physical properties have not been reported.

The high polymers of the higher aldehydes have a pronounced tendency to depolymerize and regenerate the corresponding monomer. Vogl (20) has shown, however, that these polymers can be rendered more stable if the terminal hydroxyl groups are either esterified or alkylated.

Commercial Acetal Resins

Grades and Prices. Two grades of Delrin are available: a 500 series for general injection molding and a 150 series resin for extrusion and blow molding. A higher melt viscosity, a requirement for most nonmolding operations, is provided by the extrusion-molding resin than by the injection-molding type.

Acetal resins are supplied in the form of cylindrical pellets, 0.125 in. in diameter by 0.090 in. in length. These are normally packaged in 50-lb-net special multiwall bags. In quantities of 40,000 lb or more, the price in 1961 was \$0.65 per lb. A broad array of colors is offered and prices range up to \$0.78 per lb in quantities of 40,000 lb or more.

Physical and Mechanical Properties. The fact that the acetal resins are rapidly becoming recognized as outstanding new engineering materials can be attributed to an unusual combination of properties and to the ability to retain these properties under mechanical stress and over a broad temperature range. Notable properties include: high stiffness, retention of stiffness at elevated temperatures and in the presence of many organic liquids or moisture, high tensile and impact strengths, excellent resistance to fatigue and to creep, a low coefficient of friction, good abrasion resistance, unusual electrical properties, and a high softening temperature. Properties and the tests by which they are determined are listed in Tables 1 and 2. Since modification of an acetal, as of other polymers, by fillers, diluents, plasticizers, copolymerization, and the like leads to property changes, separate tables are given for the currently available acetal resins.

Chemical Properties. One of the outstanding properties of acetal resins is resistance to attack by organic compounds. Acetal resins exhibit excellent dimensional stability and retention of properties when in contact with many organic materials. Even at elevated use temperatures, they are unaffected by most alcohols; aldehydes and ketones; ethers; esters; glycols; hydrocarbons, including gasolines and motor oils; aromatics; and many halogenated compounds. Resistance to stress cracking by these solvents is excellent. However, acetal resins can be dissolved at elevated temperatures by some classes of organic compounds—eg, phenols and substituted amides (23).

Table 1. Typical Physical and Mechanical Properties of Delrin (21)

Property	Average values for Delrin ^a		ASTM No.
	<i>500 series</i>	<i>150 series</i>	
elongation, %			
−68°F	13	38	D638
73°F	15	75	D638
158°F	330	460	D638
impact strength (Izod), ft-lb/in.			
−40°F	1.2	1.8	D256
73°F	1.4	2.3	D256
tensile strength and yield point, psi			
−68°F	14,700		D638
73°F	10,000		D638
158°F	7,500		D638
compressive stress, psi			
1% deformation	5,200		D695
10% deformation	18,000		D695
flexural modulus, psi			
73°F	410,000		D790
170°F	190,000		D790
250°F	90,000		D790
73°F, 100% rh	360,000		D790
flexural-yield strength, psi	14,100		D790
shear strength, psi	9,510		D732
deflection temp, °F			
264 psi	255		D648
66 psi	345		D648
fatigue endurance limit, psi			
70°F, 50–100% rh	5,000		
150°F, 100% rh	3,000		
water absorption, %, 24-hr immersion	0.25		D570
equilibrium, %, 50% rh	0.2		D570
equilibrium immersion, %, 77°F	0.9		
specific gravity	1.425		D792
Rockwell hardness	M94, R120		D785
flammability, in./min	1.1		D635
melting point (crystalline), °F	347		
flow temperature, °F	363		D569
deformation under load (2000 psi at 122°F), %	0.5		D621
coefficient of linear expansion per °F	4.5×10^{-5}		D696
Taber abrasion (1000-g load, CS-17 wheel), mg/1000 cycles	20		D1044
thermal conductivity, Btu/(hr)(ft ²)(°F/in.)	1.6		
specific heat, Btu/(lb)(°F)	0.35		
modulus of rigidity, psi	178,000		
Poisson's ratio	0.35		
dielectric constant, 73°F, 10 ² –10 ⁵ cps	3.7		D150
dissipation factor, 73°F, 10 ² –10 ⁵ cps	0.004		D150
dielectric strength, short time, v/mil	500		D149
volume resistivity, ohm/cm	6×10^{14}		D257
resistivity, ohm	2×10^{13}		D257
arc resistance, sec	129 (burns)		D495
permeability (P factor at 73°F) ^b			
water	1.9		
ethanol	0.2		
Freon-12 and Freon-114 (proportion 20 to 80)	>0.2		
methyl salicylate	0.3		

(continued)

Table 1 (continued)

Property	Average values for Delrin ^a ASTM No.	
	room temp	122°F
resistance to organics ^c		
carbon tetrachloride	1.2	5.7
toluene	2.6	2.8
acetone	4.9	2.6
alcohol	2.2	1.9
ethyl acetate	2.7	2.9

^a These values are representative of those obtained under standard ASTM conditions and should not be used to design parts which function under different conditions. Since they are average values, they should not be used as minimums for material specifications.

^b (g loss)(mil)/(24 hr)(100 in.²). Determined on bottles with 35-50-mil wall thickness.

^c % weight gain for 12-month total immersion. Volume change proportional to weight change.

Table 2. Typical Short-Term Physical and Mechanical Properties of Celcon (22)

Property	Average values for Celcon ^a ASTM No.		
	M-90 series	M-25 series	
elongation, %			
-30°F	25	35	D638
73°F	50	75	D638
140°F	230	280	D638
tensile impact strength, ^b ft-lb/in. ²	60	90	D1822
tensile strength and yield point, psi			
-40°F	13,700		D638
73°F	8,500		D638
160°F	5,000		D638
compressive stress, psi			
1% deformation	4,500		D695
10% deformation	16,000		D695
flexural modulus, psi			
73°F	375,000		D790
170°F	170,000		D790
250°F	80,000		D790
flexural-yield strength, psi	13,000		D790
shear strength, psi	7,700		D732
deflection temperature, °F			
264 psi	230		D648
66 psi	316		D648
water absorption, %, 24-hr immersion	0.22		D570
equilibrium, %, 50% rh	0.16		D570
equilibrium, %, continuous immersion, room temp	0.80		
Vicat softening point, °F	324		D1525
specific gravity	1.410		D792
density, lb/in. ³	0.0507		
specific volume, in. ³ /lb	19.7		
Rockwell hardness	M80		D785
flammability, in./min	1.1		D635
melting point (crystalline), °F	325		
flow temperature, °F	345		D569
deformation under load (2000 psi at 122°F), %	1.0		D621
coefficient of linear expansion per °F	4.7 × 10 ⁻⁶		D696
Taber abrasion (1000-g load, CS-17 wheel), mg/1000 cycles	14		D1044
thermal conductivity, Btu/(hr)(ft ²)(°F/in.)	1.6		
specific heat, Btu/(lb)(°F)	0.35		

Table 2 (continued)

Property	Average values for Celcon ^a		ASTM No.
dielectric constant, 73°F, 10 ² –10 ⁶ cps	3.8		D150
dissipation factor, 73°F, 10 ² –10 ⁶ cps	0.004		D150
dielectric strength, short time (20-mil film), v/mil	1,200		D149
volume resistivity, ohm/cm	10 ¹⁴		D257
arc resistance, sec	240 (burns)		D495
permeability (gas-transmission rate) at 73°F ^c			
air	1.9		
nitrogen	1.9		
oxygen	5.5		
carbon dioxide	65		
permeability (vapor transmission rate) ^d	73°F	122°F	
cyclohexanol		0.70	
hi-test gasoline	0.58	0.98	
nitrobenzene		22	
hexane		38	
benzene		84	
water	3		
toluene	3		
ethyl acetate	7		

^a These values are representative of those obtained under standard ASTM conditions and should not be used to design parts which function under different conditions. Since they are average values, they should not be used as minimums for material specifications.

^b L specimen, 1/8 in. thick.

^c Measured on 6-mil film as ml/(24 hr)(atm/mil)(100 in.²)

^d (g loss)(mil)/(24 hr)(100 in.²). Determined on 2–4 mil film or bottles with 15–33 mil wall thickness.

In general the service life of acetal resins is somewhat more limited in the presence of acids and bases than in the presence of organics. Although it can be used with dilute solutions of certain inorganics, it is not suitable for prolonged use in contact with strong acids and bases or with oxidizing agents. Thus, an acetal resin has performed well in contact with 5% acetic acid at temperatures up to 160°F, but it has degraded within six months when in contact with 10% mineral acid at room temperature. A suggested working range lies between pH 4 and 9 for aqueous solutions. Some varieties of acetal resins differ from other varieties by being highly resistant to strong aqueous bases. Parallel to the excellent solvent resistance, acetal resins exhibit resistance to many types of stains including tea, catsup, mustard, lipstick, and the like.

Water at room temperature has very little chemical effect on acetal resins. However, prolonged boiling in water results in an appreciable lowering of the molecular weight and consequent embrittlement. When immersed in water and allowed to reach equilibrium, the material absorbs 0.9% by weight at room temperature and 1.4% at 140°F. Because equilibrium is obtained only very slowly, however, absorption into most moldings is only about 0.22–0.25% in 24 hours at room temperature. This low level and rate of water absorption, which results in only small dimensional changes, means that acetal resins are suited to many applications where fluctuations in humidity would adversely affect the performance of other materials.

Acetal resins, like most thermoplastics, are affected adversely by ultraviolet light. Exposure gradually causes hazing or chalking of the exposed surface, but no

appreciable loss of mechanical properties. Prolonged exposure will reduce the molecular weight of the polymer and lead to a gradual loss of mechanical properties. For applications requiring exposure to ultraviolet radiation, photostabilized compositions are commercially available. Well-dispersed carbon black imparts very good resistance to photodegradation. Acetal resins are not attacked by microorganisms, fungi, insects, or rodents. Hence they retain their properties when buried underground. When ignited by a flame, acetal resins will burn slowly and, in this respect, are comparable to acrylics, polystyrene, and polyethylene.

Safety Aspects. In line with their general chemical inertness, acetal resins are essentially nontoxic. Feeding tests on rats in which the resin comprised 25% of the diet for a period of 90 days caused no difference in body weight or in clinical history as against the controls. Intact skin is not irritated nor does it become sensitized by the acetal resin.

In contact with water, acetal resin liberates only negligible amounts of formaldehyde and, for this reason, the National Sanitation Foundation has granted its seal of approval to Delrin. However, without the approval of the Food and Drug Administration, neither Delrin nor Celcon should be used for the packaging of food.

Fabrication and Uses

In addition to possessing an unusual combination of physical and mechanical properties, acetal resins exhibit a ready processibility and fabricability that facilitate high-volume manufacturing. By virtue of these properties, the requirements of many new industrial and consumer applications can be met more effectively by the acetal resins than by any other single family of thermoplastic resins.

Fabrication of the acetal resin into end-use articles is generally accomplished by injection molding in commercial machines or by extrusion in standard equipment into sheets, rods, tubes, and shaped profiles, or onto wire. Blow molding can be used to produce hollow articles, such as bottles. For certain special fabrication requirements, these techniques can be augmented by machining and cutting operations, such as sawing, milling, turning, drilling, reaming, shaping, threading, and tapping. These operations are carried out about as readily on the acetal resins as on the softest brasses and aluminums. Standard chip breakers on tools perform adequately in most cases.

Joining of parts into finished pieces can be accomplished in several ways, chief of which is welding. Numerous forms of welding can be practiced, such as hot-plate, gas, hot-wire, induction, and spin welding. Circular joints are readily made by spin welding. This technique consists in holding one member stationary and spinning the other against it until friction produces sufficient heat to melt the contacting surfaces. Spinning is then stopped quickly and the melted surfaces are allowed to solidify to form a welded joint. Such joints develop 80% or more of the strength of the polymer. Lap joints with shear strengths of 320 to 500 psi can be obtained by the use of rubber-base adhesives.

Articles made of acetal resins may be decorated by painting, printing, vacuum metalizing, or hot stamping. In each case, however, because of the resistance to solvents, special attention is required to obtain good adhesion of the decorative layer. A common practice is to etch the surface with an acidic agent before applying the decorative coating. Thus, excellent adhesion of paints, inks, etc, is obtained.

As of 1961, more than 550 applications of acetal resins have found commercial use. The gamut of end uses is broad indeed. A sampling of these uses follows: (1) automotive industry—gears, bearings, pulleys, instrument-cluster housings, carburetor parts, garnishes, moldings, and window crank handles; (2) building industry—door knobs, lock parts, faucet components and ball cocks, and toilet flush valves; (3) electrical industry—load-break arc chutes, communication terminal blocks, coil forms, and switch springs; (4) appliance industry—dryer parts, handles, and garbage disposal covers; (5) machine industry—pump housings, impellers, jets and venturis, pipe plugs and threaded closures, and fasteners; (6) consumer industry—electric razor cases, zippers, buckles, and sporting equipment such as fishing reels; (7) packaging industry—aerosol bottles and valves; and (8) petroleum industry—pipe for crude-oil-gathering lines and for brine disposal lines.

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ACETALS AND KETALS

Acetals (1,1-dialkoxyalkanes), $RCH(OR')_2$, and ketals, $R_2C(OR')_2$, may be regarded as the diethers of the hydrates of carbonyl compounds. Although the hydrates themselves cannot be isolated except in very special cases (chloral hydrate, for example), their diethers are reasonably stable compounds that can be prepared in the pure state, usually by reaction of an aldehyde with an alcohol. Acetals are remarkably stable toward alkalis but decompose in the presence of dilute aqueous acids, giving the original aldehyde and alcohol.

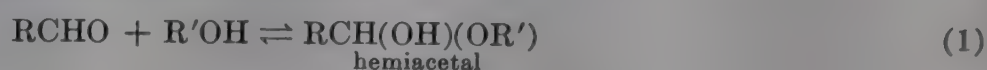
The term "acetal" denotes specifically acetaldehyde diethyl acetal, $CH_3CH(OC_2H_5)_2$. Acetals have been named in various ways (see Table 1). Cyclic acetals derived from an aldehyde and a 1,2-glycol are called *dioxolanes*. Ketals, $R_2C(OR')_2$, such as acetone diethyl acetal, are often called acetals. The sulfur analogs of acetals and ketals are called mercaptals and mercaptoles, respectively.

Table 1. Acetals

Common name	Synonyms	Formula	Mp, °C	Bp, °C	d
methylal	dimethoxymethane (IUPAC); formaldehyde dimethyl acetal; methylene dimethyl ether; formal	$CH_2(OCH_3)_2$	-104.8	44	0.8560 ²⁰
dimethyl acetal	1,1-dimethoxyethane (IUPAC); acetaldehyde dimethyl acetal; ethylidene dimethyl ether	$CH_3CH(OCH_3)_2$		64.5	0.8476 ²⁵
ethylal	diethoxymethane (IUPAC); formaldehyde diethyl acetal; methylene diethyl ether; diethyl formal	$CH_2(OC_2H_5)_2$	-66.5	89	0.8346 ¹⁵
acetal	1,1-diethoxyethane (IUPAC); acetaldehyde diethyl acetal; ethylidene diethyl ether	$CH_3CH(OC_2H_5)_2$		102-104	0.8254 ²⁰
diethyl chloroacetal	1,1-diethoxy-2-chloroethane (IUPAC); chloroacetaldehyde diethyl acetal	$ClCH_2CH(OC_2H_5)_2$		156.8	1.026 ¹⁶
2-methyl-1,3-dioxolane	acetaldehyde ethylene glycol acetal	<div>CH_3CH<div><div>O-CH₂</div><div>O-CH₂</div></div></div>		82.5	1.002 ⁹

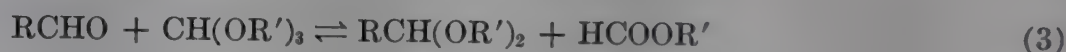
The acetals are clear, mobile liquids, lighter than water. The lower members are soluble in water, but the solubility decreases rapidly with increasing molecular weight. The lower aliphatic acetals have characteristic pleasant odors. Small quantities are found in wines and alcoholic beverages and contribute to their bouquet. These acetals are formed from aldehydes generated during the fermentation process. They are also by-products of the oxidation of alcohols, which takes place in the ageing period.

In the usual preparation of acetals from aldehydes and alcohols, *hemiacetals* are formed as intermediate products (eq 1). The reaction is exothermic and the formation of hemiacetal is indicated by changes in the refractive index and specific gravity of the alcohol-aldehyde mixture and by the disappearance of the carbonyl grouping as shown by adsorption-spectra studies. Hemiacetals (except chloral alcoholate) are difficult to isolate and they decompose on heating:



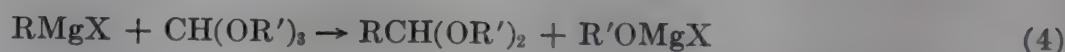
Catalysts used in this process may be acids (hydrochloric, *p*-toluenesulfonic) or salts (calcium chloride, ammonium chloride). When possible, azeotropic distillation, to remove water formed during the reaction, is employed to improve the yield. This is a general procedure when the alcohol and the aldehyde contain four or more carbon atoms.

In special cases when the usual methods fail or the acetal of an expensive or sensitive aldehyde is required, the orthoformic ester method is of great value:



This method is particularly useful for the preparation of ketals.

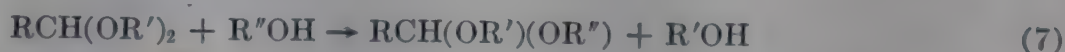
Acetals may also be obtained from orthoformic ester by use of the Grignard synthesis:



Industrially, acetals of acetaldehyde are obtained by the addition of alcohols to acetylene in the presence of boron trifluoride and mercuric oxide catalyst (eq 5) and by the addition of an alcohol to a vinyl ether in the presence of boron trifluoride (eq 6).



It should be noted that the latter reaction may give rise to mixed acetals. Mixed acetals may also be prepared by an exchange reaction between an acetal and another alcohol in the presence of an acid catalyst:



Acetals are useful in syntheses when it is necessary to protect the aldehyde group. Thus halo aldehydes may be prepared by halogenating the acetal. A number of acetals are used in the perfume industry—for example, phenylacetaldehyde ethylene glycol acetal (odor of roses) and hydroxycitronellal dimethyl acetal (lily of the valley odor). Although the odor of the acetals is weaker than and somewhat modified from

that of the corresponding aldehydes, they are used to prolong the life of perfumes because of their resistance to oxidation. Their main advantage lies in their stability in soap. The presence of alkali in soap polymerizes aldehydes to odorless resins, whereas acetals remain unattacked and retain their odor (see Perfumes).

Acetals also find industrial application as process solvents and as plasticizers. Poly(vinyl acetals) made from poly(vinyl alcohol) and aldehydes are important synthetic plastics (see Vinyl compounds, resins and plastics). Poly(vinyl butyral) is the most important material used for the interlayer in safety glass. Acetals derived from aldehydes, such as salicylaldehyde, that can undergo a subsequent coupling reaction have been used as dye intermediates.

"Acetals" in *ECT* 1st ed., Vol. 1, pp. 43-45, by Paul Bedoukian, Compagnie Parento.

ACETAMIDE, CH_3CONH_2 . See Acetic acid derivatives.

ACETANILIDE, $\text{CH}_3\text{CONHC}_6\text{H}_5$. See Acetic acid derivatives.

ACETARSONE, $\text{CH}_3\text{CONH}(\text{HO})\text{C}_6\text{H}_3\text{AsO}(\text{OH})_2$. See Arsenic compounds; Protozoal infections, chemotherapy.

ACETATE AND TRIACETATE FIBERS

Acetate fiber is a partially acetylated cellulose. It has an important place in the economics of man-made fibers in the United States. Indeed, it is third in the volume production of all man-made fibers, being surpassed only by rayon and nylon. Acetate, because of its uniform quality, color versatility, drape, hand, and other desirable aesthetic properties, finds its major applications in women's apparel and home-furnishing fabrics. Its most important nontextile use is as a filter for cigarettes.

Triacetate—an almost completely acetylated cellulose—is a relative newcomer in the realm of commercially important fibers. Among its advantages is that it is similar in many respects to the so-called true synthetics, such as acrylics, nylons, and the polyesters. It is hydrophobic and on heat treatment develops a higher degree of crystallinity, and can therefore be used to impart to fabrics such important properties as ease of care, quick drying, wrinkle resistance, and dimensional stability.

Acetate, it should be emphasized, is no longer classed as a rayon. Rayon—a regenerated cellulose—has a completely different chemical identity, a fact which was recognized by the Federal Trade Commission in December 1951. Fortisan (Celanese Corporation of America) a regenerated cellulose obtained from the saponification of acetate, is a rayon and not an acetate (see Rayon).

From a textile-product point of view, it is important to distinguish between acetate and triacetate, which are chemically similar but which represent different degrees of acetylation of cellulose. Indeed, this is recognized by the Federal Trade Commission of the U.S.A., the group responsible for enforcing Federal Law HR 469, the Textile Fiber Products Identification Act. The definition established by the FTC reads as follows: "Acetate—a manufactured fiber in which the fiber-forming substance is cellulose acetate. Where not less than 92% of the hydroxyl groups are acetylated, the term triacetate may be used as a generic description of the fiber."

History and Economic Importance

Cellulose acetate as a chemical material was known as early as 1865. The early acetates were almost completely acetylated and were therefore not soluble in any sufficiently cheap and abundant volatile solvents to be attractive for commercial use. Miles (1903) and von Bayer (1906) pointed the way to the development of the soluble acetate by removing some acetyl radicals by acid hydrolysis. It remained for Doctors Camille and Henri Dreyfus to realize the industrial importance of cellulose acetate and to develop a workable process for its manufacture. Acetate filaments were successfully spun in England shortly after cessation of World War I, and this technique was transferred to the United States in 1924. The first successful acetate filaments in the U.S. were spun in Amcelle, Maryland, on Christmas Day, 1924 (1).

The story of triacetate fiber is unique since it is the only man-made yarn that was developed to a commercial stage, failed miserably, and then became a success forty years later. In 1914, the Lustron Company in the U.S.A. produced commercial quantities of triacetate yarn, but this venture was shortlived.

Few significant publications on triacetate appeared until 1942, when Baker, Fuller and Pape (2) discussed the crystallinity of cellulose esters. Then, in 1949, two important papers appeared: one by Hinze (3), dealing with the technology of cellulose triacetate, and another by Work (4), describing the effects produced by crystallinity and orientation as shown by the use of x-ray diagrams of cellulose acetate filaments.

Considerable activity on triacetate fiber took place between 1949 and 1954 in the U.S.A. and England, which culminated (5) in a succession of rapid announcements of four triacetate fibers: Arnel (Celanese Corporation of America), October 1954; Trilan (Canadian Celanese, Ltd.), November, 1954; Tricel (British Celanese, Ltd.), November, 1954 (5a); and Courpleta (Courtaulds, Ltd.), January, 1955. The Rhodiaceta group in France and Germany also began producing triacetate in early

Table 1. United States Trademarks for Acetate and Triacetate

Trademark	Manufacturer
Acele	E. I. du Pont de Nemours & Co., Inc.
Acele Type C	E. I. du Pont de Nemours & Co., Inc.
Arnel (ta)	Celanese Corp. of America
Avicolor	American Viscose Corp.
Avisco Acetate	American Viscose Corp.
Celacloud	Celanese Corp. of America
Celacrimp	Celanese Corp. of America
Celaloft	Celanese Corp. of America
Celanese	Celanese Corp. of America
Celaperm	Celanese Corp. of America
Celarandom	Celanese Corp. of America
Celatow	Celanese Corp. of America
Celatress	Celanese Corp. of America
Chromspun	Tennessee Eastman Co.
Color Sealed (type 20)	E. I. du Pont de Nemours & Co., Inc.
Color Sealed (type 22)	E. I. du Pont de Nemours & Co., Inc.
Colorspun	American Viscose Corp.
Cycloset	E. I. du Pont de Nemours & Co., Inc.
Eastman	Tennessee Eastman Co.
Estron	Tennessee Eastman Co.
Loftura	Tennessee Eastman Co.

Table 2. Trademarks of Acetate and Triacetate Fibers of Countries Outside the U. S.

Trademark	Manufacturer and/or country
Aceta	Farbenfabriken Bayer A. G., West Germany
Albene	Société Rhodiaceta, France
Albene	S.A. Rhodiatoce, Italy
Arnel (ta)	Chemcell Fibers Ltd., Canada
Carolan	Mitsubishi Acetate Company, Japan
Celafibre	Courtaulds Ltd., England
Celafil	Courtaulds Ltd., England
Celanese	Courtaulds Ltd., England
Celcorta	Celanese Mexicana, Mexico
Celechrome	Canadian Celanese Ltd., Canada
Dicel	Courtaulds, Ltd., England
Drawinella	Wacker-Chemie G.m.b.H., West Germany
Estra	Dainippon Celluloid Company, Ltd., Japan
Fibroceta	Courtaulds, Ltd., England
Lansil	Lansil, Ltd., England
Linalbene	Deutsche Rhodiaceta A.G., West Germany
Lonzona	Lonzona-Säckingen, West Germany
Marlspun	Courtaulds, Ltd., England
Minalon	Shin Nippon Chisso Hiryo Co., Japan
Nerane	Société Rhodiaceta, France
Novaceta	S.A. Novaceta, Italy
Oceane	Société Rhodiaceta, France
Opaceta	Courtaulds, Ltd., England
Rhialin	Deutsche Rhodiaceta A.G., West Germany
Rhoa	Deutsche Rhodiaceta A.G., West Germany
Rhodia	Société Rhodiaceta, France
Rhodia	Rhodiaseta, Argentina
Rhodia	Cia. Brasileira Rhodiaceta, Brazil
Rhodiafil	Deutsche Rhodiaceta A.G., West Germany
Rhodiaflam	Société Rhodiaceta, France
Rhodia Italia	S.A. Rhodiatoce, Italy
Rhonel (ta)	Société Rhodiaceta, France
Seraceta	Courtaulds, Ltd., England
Seratelle	Courtaulds, Ltd., England
Setilose	Fabelta-Tubize, Belgium
Setina	Fabelta-Tubize, Belgium
Silene	S.A. Novaceta, Italy
Teijin Acetate	Teikoku Rayon Company, Ltd., Japan
Tenegrine	Société Rhodiaceta, France
Tri-a-Faser (ta)	Deutsche Rhodiaceta A.G., West Germany
Trialbene (ta)	Société Rhodiaceta, France
Tricel (ta)	Courtaulds, Ltd., England
Tricel (ta)	British Celanese, Ltd., U.K.
Trilan (ta)	Canadian Celanese Ltd., Canada
Trinese (ta)	Celanese Mexicana, Mexico

Legend: (ta) = triacetate.

1955. Today, tens of millions of pounds of triacetate are sold in the United States, England, and Europe.

The economic importance of acetate and triacetate is illustrated by the list of trade names in Tables 1 and 2, and by the 1960 production figures and 1962 capacity shown in Table 3 (18).

Table 3. Plant Location and Acetate Filament Yarn Production by Country

Country	Company	Plant location	Filament	Staple	Millions of pounds	
					1960 Production	1962 Capacity
Argentina	Rhodiaceta, Argentina, S.A.	Quilmes	x	x	3	4
Australia	Courtauld's (Australia) Ltd.	Tomago, N.S.W.	x		3	4
Belgium	"Fabelta" (Union des Fabriques Belges de Textiles Artificiels S.A.)	Tubize	x			
Brazil	Cia. Brasileira Rhodiaceta, Fabrica de Rayon; Industrias Reunidas F. Matarazzo S.A.	Santo André, São Paulo; Agua Branca, São Paulo	x x	x }	12	13
Canada	Canadian Celanese, Ltd.; Canadian Chemical Co., Ltd. (fiber sold by Chemcell Fibers, Ltd.)	Drummondville, Quebec; Edmonton, Alberta	x x ^a	x ^a } x ^a }	21	28
Colombia	Celanese Colombiana, S.A.	Yumbo, near Cali	x	x	6	8
Cuba	Acetafil, S.A.	Wajay	x	x	0	3
France	Société Rhodiaceta	Lyon-Vaise (Rhône), Roussillon (Isère)	x x ^a	x } x }	15	20
West Germany	Deutsche Rhodiaceta A.G.; Lonzona, Gesellschaft für Acetatprodukte m.b.H.; Wacker-Chemie G.m.b.H.; Farbenfabriken-Bayer A.G.	Freiburg/Br.; Säckingen/Baden; München-Burghausen; Dormagen	x x	x } x }	10	12
India	Sirsilk, Ltd.	Sirpur-Kaghaznagar Andhra Pradesh	x		4	8
Italy	Chatillon S.A. Italiana per le Fibre Tessili, Artificiali; Società Novaceta; Società Rhodatoce	Vercelli; Magenta; Pallanza (Novara)	x x x	x } x } x }	24	25

Japan	Dainippon Seruroido KK (Dainippon Celluloid Co., Ltd.);	x	x	30	45
	Mitsubishi Rayon KK (Mitsubishi Acetate Co., Ltd.);				
	Nichitsu Acetate KK (Nichitsu Acetate Co., Ltd.);				
	Shin Nippon Chisso Hiryo KK (New Japan Nitrogenous Fertilizer Co., Ltd.);				
	Teikoku Jinzo Kenshi KK (Teikoku Rayon Co., Ltd.)	x ^a	x	15	20
Mexico	Celanese Mexicana, S.A.	x		1	2
Peru	Filamentos Sinteticos, S.A.	x		1	2
Spain	Industrias del Acetato de Cellulosa, S.A. (INACSA)				
U.K.	British Celanese, Ltd. (subsidiary of Courtaulds);	x ^a	x ^a	45	70
		x ^a			
		x			
		x			
	Lansil, Ltd.;	x			
	Nelsons Silk Ltd.				
U.S.A.	American Viscose Corp., Fibers Division;	x	x ^a	228	318
	Celanese Fibers Company;	x ^a			
	E. I. du Pont de Nemours & Co., Inc.;	x			
	Tennessee Eastman Co., (Div. of Eastman Kodak Co.)	x			
Uruguay	Urace, S.A.	x		2	2.5
Venezuela	Celanese Venezolana, S.A.;	x	x	6	8
	Sudasetta, C.A.	x			
Total				429	595.5

^a Also triacetate.

NOTE: Little information is available on the manufacture of acetate in the U.S.S.R. However, *Chem. Eng. News*, July 31, 1961, p. 130, states that "The U.S.S.R. has included an acetate plant in their current seven-year plan. This plant is to be located in Uzbek."

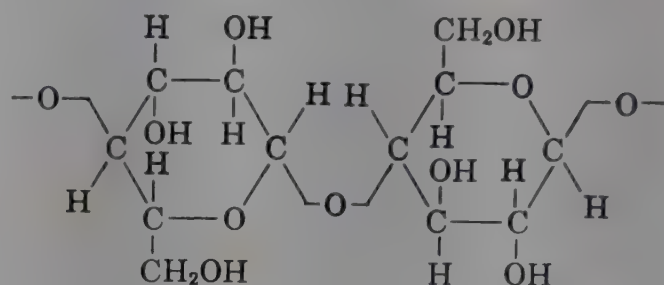
The prices of acetate and triacetate staple fiber are higher than for rayon and cotton but considerably lower than for nylon, acrylic, and polyester fibers. In general, the prices of filament yarns of acetate and triacetate are considerably lower than for nylon and the polyesters.

Chemical Reactions and Composition

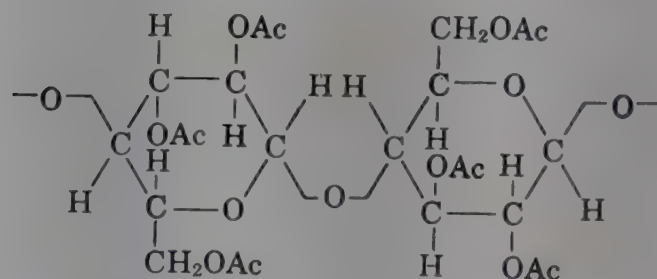
The basic building unit of the cellulose molecule, the cellobiose residue, is made up of two glucose residues (see Fig. 1a). Each glucose residue contains three hydroxyl groups, which are acetylated by reaction with acetic anhydride,



The triacetate of cellulose would therefore have the structure shown in Figure 1b, although it may be noted that acetylation is not quite complete, and the commercial product is not a precise chemical entity.



(a) Repeat unit of cellulose; cellobiose residue.



(b) Repeat unit of triacetate.

Fig. 1. Comparison of structures of cellulose and triacetate.

From a material balance point of view, one pound of cellulose requires 1.89 lb of acetic anhydride to produce 1.78 lb of triacetate, plus a recoverable by-product of 1.12 lb of acetic acid.

Acetate flake is obtained by partially deacetylating the triacetylated cellulose, giving a product, known as *secondary acetate*, which has approximately $2\frac{1}{2}$ acetyl groups per glucose unit. It is believed that the acetyl groups removed are those on one of the secondary hydroxyls, rather than the primary hydroxyl, of the glucose unit, and therefore acetate fiber contains some fully acetylated glucose units (as shown in Fig. 1b) and about an equal number of glucose units acetylated on the primary hydroxyl plus one of the secondary hydroxyls.

In characterizing the degree of acetylation, "percent acetyl value" and "percent combined acetic acid" are both used. Since the formula weights are CH_3CO , 43, and

$\text{C}_6\text{H}_7\text{O}_5\text{COOH}$, 60, the two figures are always in the ratio 43/60. Their relation to the number of hydroxyls acetylated per glucose residue is:

<i>Acetyls per glucose</i>	<i>Percent acetyl value</i>	<i>Percent combined acetic acid</i>
2	29.8	40.7
2.5	37.5	57.0
3	44.8	62.5

Commercial triacetate fiber has a combined acetic acid content of 61.5%, corresponding to 34 hydroxyls acetylated out of 35.

Physical and Chemical Properties of Acetate and Triacetate Flake. Acetate and triacetate flake are the materials from which the fibers are produced by extrusion. Nonfiber acetates are white amorphous solids which can be produced in granular, flake, or powder form by varying the process of preparation. (See Cellulose derivatives.)

The commercial products do not have sharp melting points. Secondary acetates begin to soften at approximately 220°C, but as the degree of hydroxyl substitution is increased, the melting point rises. The densities of flake cellulose acetates vary with physical form and range from 10 to 30 lb/ft³ for materials stored or shipped in loose bulk. The solubility of various acetates is affected by the acetyl value. In the manufacture of fibers and cast films, acetone is used as a solvent for secondary acetate, and such solvents as methyl acetate, dimethyl formamide, and some chlorinated hydrocarbons for triacetates.

A reduction of the cellulose polymer chain length occurs during acetylation and hydrolysis. The normal industrial practice includes maintaining reaction conditions that will result in a product with a specific average degree of polymerization. The requirement depends on the end use of the polymer, and it is usually specified as some form of viscosity measurement. In a 20% solution in 90/10 acetone/ethanol, the average viscosity of a fibers-grade secondary acetate approximates 275 poise. In this instance, the degree of polymerization of the purified cellulose has been reduced to one-fourth of the original value. Lower polymers of secondary acetate are marketed for the plastics industry with viscosities ranging from 65–200 poise by the same method of measurement. The degree of polymerization is controlled independently from the acetyl value; however, the viscosity of acetate solutions is affected by the acetyl value.

The degree of hygroscopicity of various cellulose acetates depends on the acetyl value. This property has commercial significance because of the relationship to shipping costs and the properties of fibers and plastics. The equilibrium moisture-regain level of material having a combined acetic acid content of 54.5% under conditions of 70°F and 65% relative humidity is 6.3%. The corresponding value for triacetate is 3.5%.

Acetate will hydrolyze in the presence of aqueous alkalies. Acetate fiber can be converted commercially by hydrolysis to a regenerated cellulose fiber which is chemically similar to rayon (and in textile terminology is called a rayon). Such yarns are marketed under the trade name *Fortisan*. Strong acids and alkalies decompose cellulose acetate.

Manufacture of Cellulose Acetate Flake

In the preparation of acetate fiber from acetate flake, a relatively concentrated solution of the polymer is to be extruded through a small orifice. Since the solution is of high viscosity it is necessary that it does not exhibit serious thixotropy, and that it be free of small fibers and dirt. Since an enduring fiber is to be the end product, the cellulose acetate must be stable. These considerations affect not only the method of manufacture of the cellulose acetate but also the selection of raw materials.

Purified cellulose made from wood or cotton is used in the preparation of cellulose acetate. From a chemical aspect, cotton is the purest natural form of cellulose. Cotton is grown primarily for textiles in which the long staple length produced by ginning is used. The shorter, more chemically reactive, cotton fibers represent a by-product and are recovered as linters cut from the cottonseed (see Cotton; Cottonseed). The purity advantage of chemical cotton over wood cellulose is offset by an unstable price and availability situation; this makes chemical cotton economically unsatisfactory for use in the cellulose acetate industry. Currently, therefore, cotton as a source of cellulose has largely been replaced by wood pulp, except to obtain cellulose acetate for plastics, where color is very important.

Almost any plant that grows contains sufficient cellulose to be utilized as a source of chemical cellulose. The fast-growing coniferous trees, such as pine, hemlock, and spruce, are currently the most-used source of cellulose, because of the regularity of supply and the reasonable uniformity of price and quality. The purified cellulose must be relatively free of hemicelluloses and polysaccharides, such as mannans and xylans, which may contribute to serious thixotropy, and of oxycelluloses, which may form metallic salts that could cause orifice blockage. An important measure of cellulose purity is the alpha-cellulose content, which ranges from 94–99% in a satisfactory material (see Cellulose).

The same considerations of purity, uniformity, and price stability apply to the other raw materials for the cellulose acetate process. As a result of the growth of the chemical industry, however, it is relatively easy to get pure acetic acid, acetic anhydride, catalysts, and solvents.

Two methods are commonly used to prepare cellulose acetate for the fibers industry. In one, the acetylation with acetic anhydride is carried out in the presence of glacial acetic acid; in the other, known as the *solvent process*, glacial acetic acid is replaced by methylene chloride.

The commercial technique used is to acetylate completely during the dissolving step and then to hydrolyze the cellulose acetate (while it is still in solution) back to the required acetyl value. The process may be broken down into four main steps: (1) pretreatment, (2) acetylation, (3) hydrolysis, and (4) recovery of cellulose acetate and solvents. A schematic flowsheet of the process (in which acetic acid is used as the solvent) is shown in Figure 2.

Pretreatment. Purified cellulose is received in sheets (see Pulp) by the acetate manufacturer. This is a commercial product, prepared by chemical treatment of either wood or cotton linters; for economy in shipping, the purified fibers are dried and compressed. Prior to acetylation, the fibers in the pulp must be opened and dispersed to present the largest possible surface area in the reaction mixture. Mechanical opening is achieved by feeding the cellulose through an attrition mill. Opening is followed by a pretreatment chemical activation, which swells the cellulose fibers.

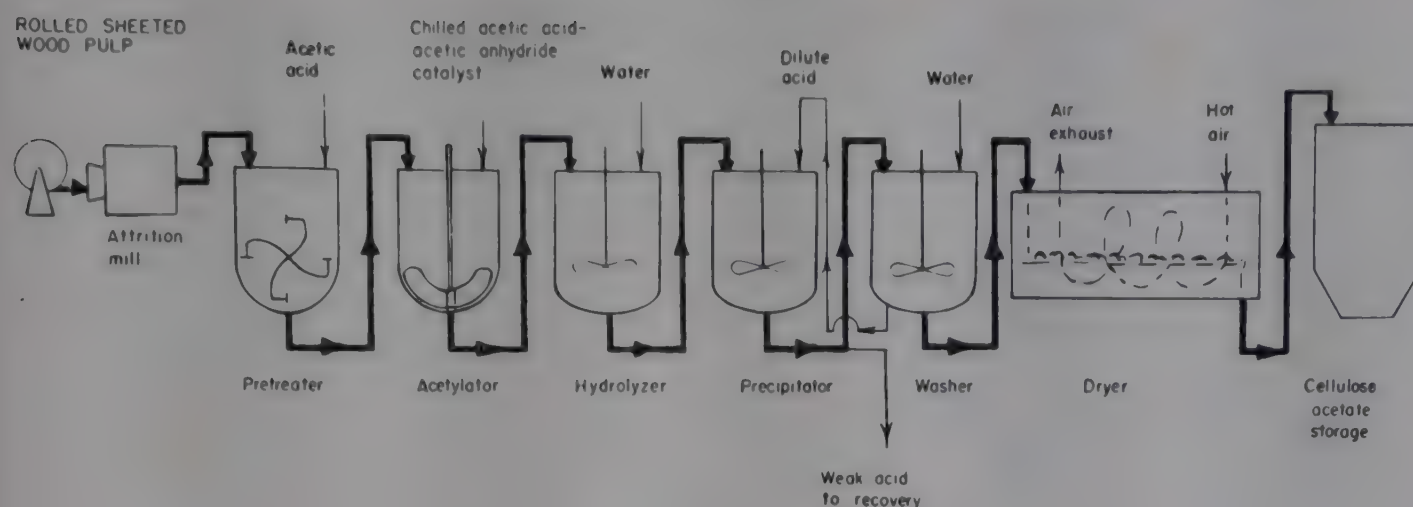


Fig. 2. Cellulose acetate manufacture.

Some chain fission also occurs at this point. Many pretreatment agents are available, but acetic acid is most commonly used. Pretreatment, therefore, consists of mechanically agitating a 1:3 weight ratio mixture of glacial acetic acid and cellulose. The resulting mixture closely resembles the original shredded cellulose in physical appearance.

Acetylation. After transferring the pretreated cellulose into the acetylation equipment, the necessary reagents for esterification are added. Batch equipment is ordinarily used, although the patent literature indicates that continuous operation has received some attention (6-15). A satisfactory batch vessel requires a heavy-duty stirrer, or kneader, and cooling.

The quantity of acetic anhydride used for acetylation is usually 5-10% in excess of that required to react with the cellulose and with the water content of the pretreated mixture. The amount of acetic acid added, together with the acid already in the pretreated cellulose plus the acid produced by the reaction, is sufficient to give a 15-25% final concentration of cellulose acetate. Sulfuric acid in amounts ranging up to 15%, based on the weight of the cellulose, is employed as a catalyst to promote the reaction. Small amounts of perchloric acid may be substituted for sulfuric acid as a catalyst (16). In the solvent process, methylene chloride is substituted for the acetic acid.

The acetylation reaction is exothermic; the amount of heat liberated is approximately equivalent to the heat of hydrolysis of acetic anhydride. Since jacketed vessels do not have sufficient cooling capacity to maintain adequate temperature control of large batches, additional cooling is necessary. This is achieved by prechilling the acid and anhydride mixture, in a separate jacketed vessel called a crystallizer, until the acetic acid freezes to give a slurry in the anhydride. The heat of fusion of the glacial acetic acid acts as a coolant dispersed uniformly in the reaction mixture, thus providing better control of the highly exothermic reaction. In the solvent process, refluxing of the methylene chloride provides the cooling.

Several competing reactions occur during acetylation. These are described by Malm and Hiatt (17). Sulfuric acid and acetic anhydride will react to form acetyl-sulfuric acid,



Acetylsulfuric acid rearranges to sulfoacetic acid, $\text{HO}_3\text{SCH}_2\text{COOH}$, at elevated temperatures, but commercial acetylation conditions do not favor the rearrangement.

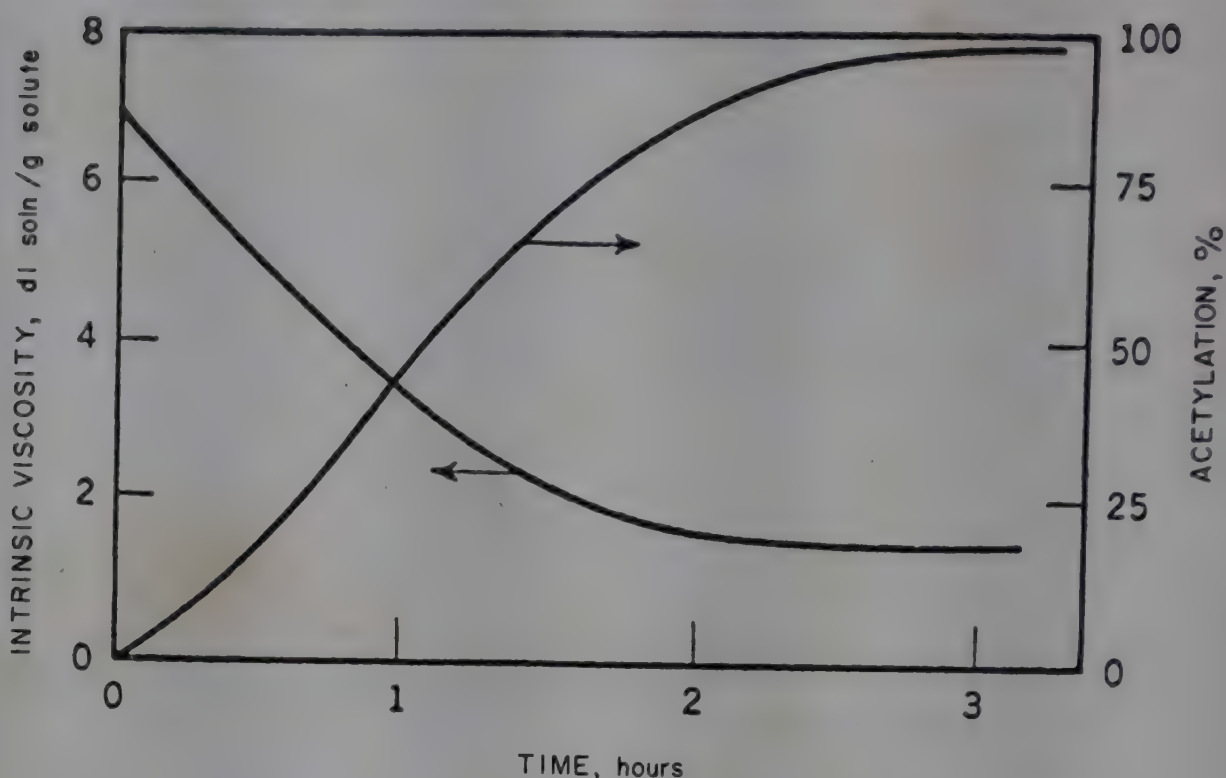


Fig. 3. Changes in the intrinsic viscosity of cellulose during acetylation.

Sulfuric acid reacts with cellulose, replacing —OH groups with sulfate groups, $\text{—OSO}_3\text{H}$. However, during acetylation, most of the sulfate groups are replaced by acetyl groups. At completion of esterification, most of the remaining sulfate groups are located at the primary hydroxy position on the cellulose. If the intermediate stages are overlooked, the net results of the acetylation process are (1) the reaction of the hydroxyl groups of the cellulose with the acetylating material, resulting in cellulose acetate and acetic acid, and (2) the fission or splitting of the cellulose chain, a reaction which leads to the lowering of the intrinsic viscosity. Catalyst, time, and temperature promote both reactions. The goal is, of course, to complete the acetylation with the desired viscosity. The course of these two competing reactions may be expressed graphically (see Fig. 3). Since the chain fission (reaction 2) is accelerated by temperature, particularly in the presence of large amounts of catalyst, temperature control is very important; by and large, temperatures in excess of 50°C are avoided.

As the acetylation reaction progresses the physical appearance of the batch gradually changes from a mass of shredded fibers, through an opaque, doughlike stage, to, finally, a clear, highly viscous solution. The acetyl value at completion is slightly less than 44.8%, the value for fully acetylated cellulose. Some of the sulfuric acid catalyst is combined with the cellulose (19) and must be removed during hydrolysis in order to provide a stable product.

Hydrolysis. The acetylation reaction is stopped by adding sufficient water to react with the remaining acetic anhydride and to give a water content of 5–30%. To prevent localized precipitation, dilute aqueous acetic acid is used. The rates of sulfate-group and acetyl-group removal are controlled by time, temperature, and acidity of the solution.

Optimum conditions for sulfate-group removal are not the same as for acetyl hydrolysis. Therefore, in some processes, a two-stage hydrolysis is advantageous. The usual procedure is to remove sulfates first under relatively strong acid conditions, which promote a certain amount of depolymerization. After most of the sulfate groups have been hydrolyzed, acetyl hydrolysis proceeds with a much slower rate of

depolymerization. As temperature is increased, the rates of both types of hydrolysis increase. In commercial practice, the temperature during hydrolysis may exceed 100°C and the time required will vary from 1 to 8 hours depending on the conditions used and the acetyl value required in the final product. When the desired acetyl value of the cellulose acetate is reached, the remaining catalyst is neutralized by adding sodium acetate or magnesium acetate. (It will be seen that "neutralizing" refers to neutralizing only the sulfuric acid, not the acetic acid.)

Precipitation, Washing, and Drying. After hydrolysis the cellulose acetate is precipitated from solution by adding water. After draining excess weak acid, the precipitated flake is washed, usually in two stages. Weak acids from these steps can be used as makeup for other stages of the process or may be recovered for reuse. The precipitated cellulose acetate is then washed with additional water until neutral, and dried to the desired moisture content.

Acetate flake is conveniently stored or shipped in bulk by trailer truck or railroad freight car. Small quantities are packaged in multiwall paper bags. If protection against change in moisture content due to atmospheric humidity is required, the bags may include a vapor-barrier layer.

Preparation of Triacetate. The preparation of the triacetate differs from the preparation of secondary acetate in that there is little hydrolysis of acetyl groups in the hydrolysis step. In processes in which sulfuric acid is used as a catalyst, magnesium acetates and water (20,21) are added slowly, and temperatures in the range of 50–100°C are employed, the removal of sulfate groups and their partial replacement by acetyl groups can be accomplished. Commercial triacetates of 61.5% combined-acetic acid content can be achieved. The magnesium salt removes the sulfuric acid as the relatively insoluble magnesium sulfate.

When methylene chloride is used as the solvent in the manufacture of triacetate, very small quantities of sulfuric acid, as low as 1% based on the weight of cellulose, may be used. The small amounts of combined sulfates formed can be removed by a very mild hydrolysis yielding triacetates of approximately 62% combined acetic acid. Perchloric acid may be used as a catalyst; it gives triacetates of nearly theoretical acetyl values.

The *Schering process* (also known as the *nonsolvent process*, or *fibrous process*) (22) is used in Germany for the manufacture of triacetate. In this process, solution of the reacting cellulose during acetylation is prevented by the use of a nonsolvent medium, such as benzene. The normal catalyst is perchloric acid, and triacetates of theoretical acetyl value are obtained. The product has very much the appearance of the original cellulose.

Recovery of Acetic Acid. Acetic acid recovery is carried out principally by a modified Suida solvent-extraction process. In both the acetic and methylene chloride methods of manufacture, it is necessary to convert recovered acetic acid to acetic anhydride. Catalytic pyrolysis gives good yields at low cost (see Ethanoic acid).

Manufacture of Acetate Fibers

The various processes for converting cellulose acetate flake into fiber form are commonly described as *spinning*, but more accurately as *extrusion*. The *dry extrusion* process accounts for most of the yarn produced. By this method, cellulose acetate dissolved in a volatile solvent is pumped through a multihole spinneret into a column

of warm air where the fibers are formed by evaporation of the solvent. The *wet extrusion* process employs a similar cellulose acetate solution; however, fiber formation is accomplished by a solvent/water bath which has the effect of precipitating the acetate from the solution. In the *melt extrusion* process, the polymer is heated until molten and extruded into room-temperature air to produce fibers.

After extrusion, one or more of several textile operations may be performed on the extruded fiber. These may involve stretching or drawing to increase strength, twisting to enhance resistance to damage or to effect changes in fabric styling, and various winding operations to provide a package suitable for shipping.

The dry-extrusion process for cellulose acetate consists of four main operations: (1) Dissolving the cellulose acetate in acetone, (2) removal of insoluble material by filtration, (3) extrusion of fibers and winding onto a suitable package, and (4) mechanical textile operations on the extruded yarn.

Acetone, which is a relatively cheap material, is universally used as a solvent for secondary acetate in the dry-extrusion process. If water is added to the acetone, the viscosity of acetate solutions passes through a minimum at the 90:10 ratio of acetone to water. Economy of operations requires the maximum solids concentration and minimum viscosity. However, optimum fiber properties are a limiting factor, and the specifications for an acetate solution are necessarily a compromise. Higher solids concentrations produce fibers with better properties, however, solution viscosity increases rapidly as the polymer concentration increases, and a practical limit is quickly reached. The patent literature indicates common use of 25% concentration of cellulose acetate in 95–98% acetone and 5–2% water.

Heavy-duty mixers or tumbling dissolvers are required to prepare the solution. Since acetone presents a fire hazard at relatively low concentrations (2.5%) in air, the operations through extrusion are continuous and enclosed. Precise control of cellulose acetate concentration is required in order to extrude fibers with uniform weight per unit length. The acetone–water ratio also requires close control because of its influence on fiber properties, such as tensile strength and elongation. The uniformity of solution viscosity is less important, because the solution is delivered to the spinneret by a positive-displacement pump.

There is an interesting sidelight on the relationship of the apparent viscosity of concentrated cellulose acetate solutions to the cellulose used. At a given concentration for cellulose acetates of identical intrinsic viscosities, the cellulose acetate made from wood pulp has a higher apparent viscosity than the product made from cotton linters. It has been found that this is the result of a thixotropic effect, probably due to the presence of certain polysaccharides in the original pulp. However, under a shear stress of greater than 3000 dynes per square centimeter (which is the shear in pumping or filtration) the two solutions have identical viscosities and behave identically in plant operations.

Successful extrusion of the filaments requires that the cellulose acetate solution be passed through fine holes which may range in diameter from 30 to 60 microns. Cleanliness of the solution is a prerequisite and necessitates several stages of filtration.

The principle of extrusion is simple in conception, but the precision of the operation reflects the ingenuity of engineering. In outline, a well-filtered, uniform, preheated solution is delivered to the spinneret at constant volume. Accurate, durable metering pumps are necessary to assure extrusion of fibers with uniform physical properties. Spinnerets which may have from thirteen to several hundred holes are

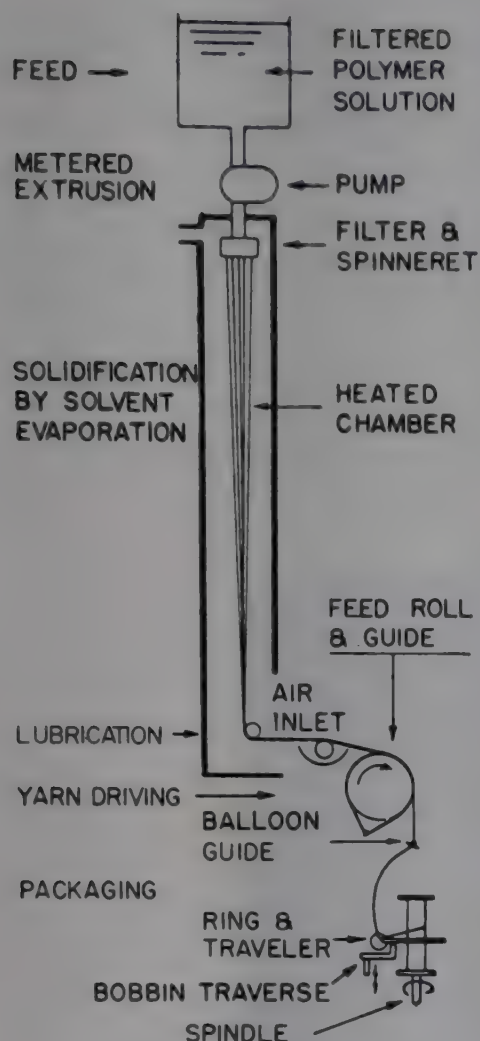


Fig. 4. Dry extrusion. Dry spinning of cellulose acetate fibers (23).

precision-made to close tolerances for size and shape. A schematic flow diagram of the extrusion process is shown in Figure 4.

The heated polymer solution is extruded into a column of warm air. Filaments emerging from a spinneret are shown in Figure 5. The column or cabinet length may range from 6 to 25 feet, depending on the drying capacity required. The direction of airflow may be countercurrent or cocurrent with the direction of fiber travel. In some cases air enters at the top and at the bottom of the cabinet, and is withdrawn from the middle. The principal characteristics of multifilament fibers are dependent on the rate of drying, which therefore demands precise control of airflow and temperature.

The fiber is wrapped around a metering roll and this is pulled through the cabinet at a controlled rate. The relationship between the metering pump output and the metering roll feed rate controls the weight per unit length or denier of the yarn. The yarn is made by taking together the individual filaments from all of the orifices in one spinneret, and giving them a certain amount of twist as they are wound upon the spindle. Such a product is a *continuous-filament yarn* (as distinguished from *staple*, see p. 123). Cellulose acetate yarn sizes in the range from 45 to above 1000 denier are produced. (Denier, which is a measure of linear density, is defined as the weight in grams of a 9000-meter length of yarn.)

Yarns must be lubricated for successful processing. The lubricant is applied precisely, in amounts ranging from 1 to 5%, by an applicator positioned just beyond the point where the yarn emerges from the cabinet. Several different lubricants are used, depending on the type of application intended for the yarn. The solvent vaporized in the extrusion process is usually recovered by adsorption on activated

carbon. It is removed from the carbon by steam distillation and is then purified by distillation in fractionating columns.

The process for the extrusion of triacetate fibers is essentially the same as for acetate, except for the solvent employed. As the degree of hydroxyl substitution increases, acetone solubility of the acetate flake decreases. Triacetate is not soluble in acetone, but it is soluble in methyl acetate, glacial acetic acid, dimethyl formamide, dimethyl sulfoxide, and some chlorinated hydrocarbons.

Acetate can be wet-extruded into aqueous or other nonsolvent baths to obtain yarns with special properties. The extrusion solution may be either (1) the solution used in dry extrusion, ie, acetate dissolved in acetone, or (2) the acetic acid solution of the acetate after hydrolysis.



Fig. 5. Dry extrusion. Filaments emerging from spinneret.

A relatively small amount of triacetate yarn has been made by melt spinning. Special techniques are necessary to prevent degradation at the high temperatures at which triacetate melts. The basic principle of these techniques is to hold the material in the molten state for only a short time.

Types of Yarns and Fibers. A wide variety of different yarn sizes and types are produced. In addition to the range of deniers, the number and shape of individual filaments may be changed. For example, 75-denier yarns are marketed, containing from 17 to 50 filaments and thus providing a choice of denier per filament (den/fil) from 1.5 to 4.4. Products ranging from 1 to 16 den/fil have been produced. Most yarns are in the 3–4 den/fil range.

The cross-section shape can be changed by using different shapes of spinneret holes. Dry extrusion through round holes provides filaments with a roughly round shape having serrated edges. A triangular hole produces filaments in the form of a three-pointed star. Variations of the filament shape from a given type hole can be achieved by changing the temperature conditions at extrusion.

Continuous-filament yarns are produced on machines operated as individual units which may have from 15 to over 100 extrusion units. The full bobbin or package is removed on a time-schedule basis and may contain from one to several pounds of yarn, depending on the type and size of the extrusion take-up device. The extruded yarn is usually transferred to a different package for shipment. It is common to insert twist ranging from 0.8 to 20 turns per inch in the final product.

Yarn Packages. The textile industry is exceedingly complex and requires many different types of packages. As it is beyond the scope of this article to provide comprehensive coverage, only cones and beams, two common shipping units for continuous-filament yarns, are described.

Cones may contain from one to eight pounds of yarn. The cone tube, which forms the base for the package, normally has a length of approximately $7\frac{1}{2}$ inches, a base diameter of 2 inches, and a top diameter of $1\frac{1}{4}$ inches. Since the yarn is withdrawn over the top of the cone, the tip of the cone tube must have a smooth, usually lacquered, finish to preclude damage to the yarn. During the coning operation the yarn is traversed approximately once per three spindle revolutions. At the start of cone winding, a magazine wrap is provided so that the consumer can effect an automatic transfer to a second cone with minimum effort and downtime. Cones are shipped in cases containing from several to many units. A common arrangement is to pack 96 four-pound cones in a single case.

Beams are large spools of yarn varying in length from 21 to 84 inches and with flange diameters from 21 to 36 inches. Beams are usually constructed of aluminum alloy. When filled, a beam may hold several hundred pounds of yarn. The most common size of beam used by the tricot knitting trade measures 42 inches in length and 21 inches in diameter. Section beams for weaving are usually 54 inches long and 30 inches in diameter. In both types of beams, several hundred yarn ends (that is to say, several hundred separate yarns) are wound parallel and simultaneously. A beam may contain as many as 2400 individual yarn ends. The length of yarn on beams varies with the beam capacity and the intended end use. Lengths ordinarily vary from 12,000 to 85,000 yards. When beam winding is completed, the ends are taped in position and a cover wrap is put in place. For shipping, the beams may be packed individually in cartons or in steel racks holding two or four beams.

Staple. Slightly less than 20% of the total output of acetate and triacetate is marketed as staple, that is, cut into short lengths, resembling the short fibers of cotton. This is achieved by a variation of the treatment of the extruded fibers. Instead of having the output of each spinneret wound into a yarn on individual packages, the filaments from several spinnerets are all gathered together into a tow, which is passed through a mechanical crimping device and then cut into short lengths, usually $1\frac{1}{2}$ to 2 inches, in a continuous operation. Acetate staple is shipped in bales weighing 400 to 800 pounds. Most of this fiber is spun into yarn by the cotton system.

Properties

Fiber Structure. Acetate is characterized by a relatively low degree of orientation and crystallinity. The crystallinity of acetate is changed very little by heat treatment. On the other hand, triacetate develops considerable crystallinity on treatment with heat. X-ray diffractions show this clearly. Figure 6 represents a diffraction pattern of Arnel triacetate (Celanese Corporation) extruded without heat

treatment. Figure 7 shows the diffraction pattern of a yarn which was heat-treated for 30 seconds at 240°C, while held at constant length. As can be seen, the diffraction arcs due to scattering from the various crystal planes of the triacetate crystallites begin to separate; they also become sharper and more intense, indicating a higher crystalline order. The reaction of triacetate to heat treatment is responsible for many of the differences in properties between acetate and triacetate (23a,23b,39).

Appearance and Color. Acetate and triacetate fibers and yarns are produced principally in two gradations of luster—bright and dull. The dull yarn contains 1 to 2% of an added delustrant, eg, titanium dioxide, whereas the bright yarn contains no delustrant. The degree of light absorption of both bright and dull acetate and triacetate is almost constant over the visible range of the spectrum, becoming slightly greater near the ultraviolet portion. Light reflected from dull yarn is nearly all

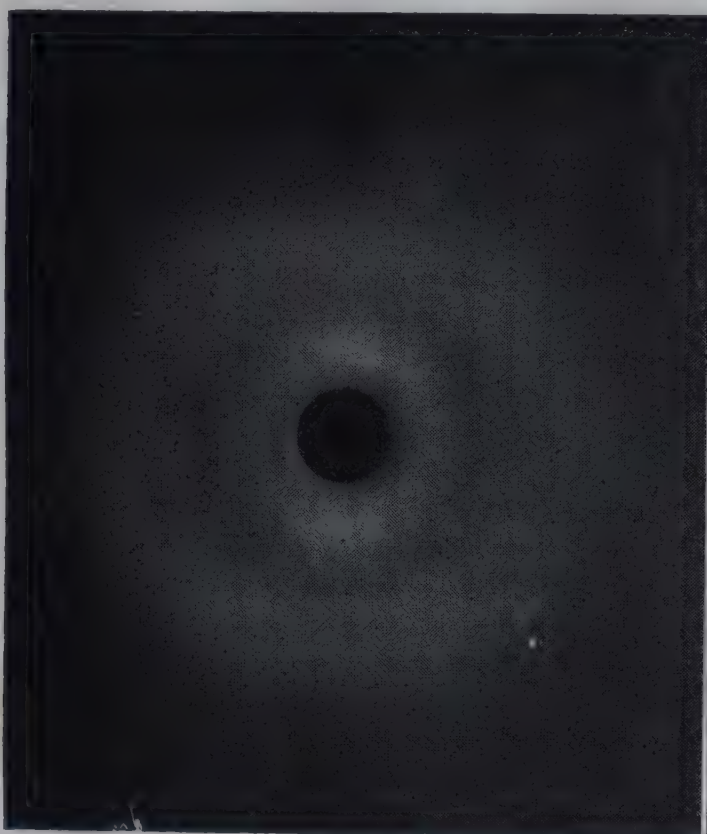


Fig. 6. X-ray diffraction pattern of triacetate not treated with heat.

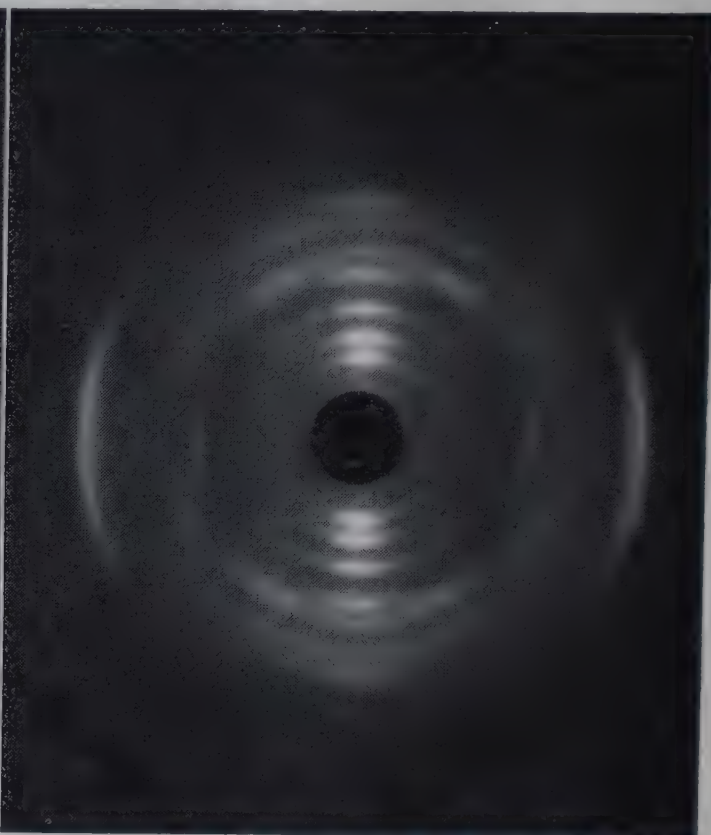


Fig. 7. X-ray diffraction pattern of heat-treated triacetate (240°C, 30 sec).

diffuse; whereas with bright yarn, a significant amount of specular (mirrorlike) reflection is noted. The ratio of specular to diffuse reflection decreases with increasing yarn twist, as a result of surface distortion.

Acetate and triacetate fibers and yarns may be produced with an exceptionally high degree of whiteness (24), depending on the purity of the cellulose and the control of manufacturing procedures. This whiteness contributes to the ability of the dyer to obtain clean, pure colors in a wide range of shades and depths. Whiteness is not significantly altered by exposure to indoor climatic conditions over long periods of time.

Solution-dyed fibers and yarns (see p. 135) are characterized by an exceptionally high degree of colorfastness to such agents and to treatments such as washing, dry-cleaning, sunlight, perspiration, sea water, and crocking. Perhaps most important is the virtual elimination of fading caused by gases or fumes (including oxides of nitrogen and ozone) prevalent in certain sections of the world. This type of fading may be

experienced with acetate or triacetate dyed in the conventional manner unless inhibitors are used.

Specific Gravity. The apparent specific gravity of any fiber is dependent to some extent on the medium used in the determination. Results may vary due to fiber swelling and perhaps due to improper wetting of the total fiber surface. A study of the use of various immersants for acetate by Fortress (25) gives values ranging from 1.306 to 1.415. However, a study of the literature shows that the most generally accepted specific gravity for both acetate and triacetate is 1.30.

Refractive Index. The refractive index parallel to the fiber axis E is 1.478 for acetate, 1.472 for triacetate. The index perpendicular to the axis W is 1.473 for acetate, 1.471 for triacetate. The difference between E and W (birefringence) is very low for acetate and practically nondetectable for triacetate.

Absorption and Swelling Behavior. Typically, the absorption of moisture by acetate and triacetate is dependent on the relative humidity to which the fibers are exposed. It varies, however, depending on whether equilibrium is approached from the dry or the wet side. This effect—referred to as hysteresis—is noted over the entire range of relative humidities and is clearly shown in Table 4.

Table 4. Regains,^a %, of Acetate and Triacetate on Absorption and Desorption at 22°C (26)

Rh, %	Acetate		Triacetate	
	Absorption	Desorption	Absorption	Desorption
9	0.8	1.0	0.5	
22	1.9	2.4	1.2	
33	2.7	3.5	1.8	2.2
44	3.7	4.9	2.5	3.3
53	5.0	6.2	3.3	4.3
65	6.3	8.0	4.2	5.4
76	7.9	10.2	5.6	7.0
86	10.3	12.1	6.8	8.4
94	13.0	14.0	8.8	9.7
100	19.0	14.0	12.5	

^a Term used to denote moisture content of textile materials (see 27).

Additional moisture regain isotherms for acetate have been published by Whitwell and co-workers (28). Heat-treated triacetate has a lower regain than nonheat-treated fiber, and values in the range of 2.5–3.2% have been reported (29,30).

In the U.S.A. “commercial regain” is used to calculate commercial weights of yarns or fibers. In effect, commercial regain is added to the weight of bone-dry fiber to account for the moisture normally found in textile fibers. The figure for percent commercial regain, as taken from ASTM D 1909-61 T, ref. 10, is 6.5 for acetate and 3.5 for triacetate. In Europe and in other parts of the world the BISFA (Bureau International pour la Standardisation des Fibres Artificielles) rules (31) are used for determining the commercial weight of acetate and other man-made fibers. The basic premise differs from that of the ASTM (American Society for Testing Materials) in that the BISFA rules include not only a figure to account for the moisture normally found in fibers, but also a figure for the normal finish present on the fiber as shipped. Thus, the commercial weight of acetate according to the BISFA rules includes a figure of 9%, based on the bone-dry finish-free weight of the fiber. On the other hand,

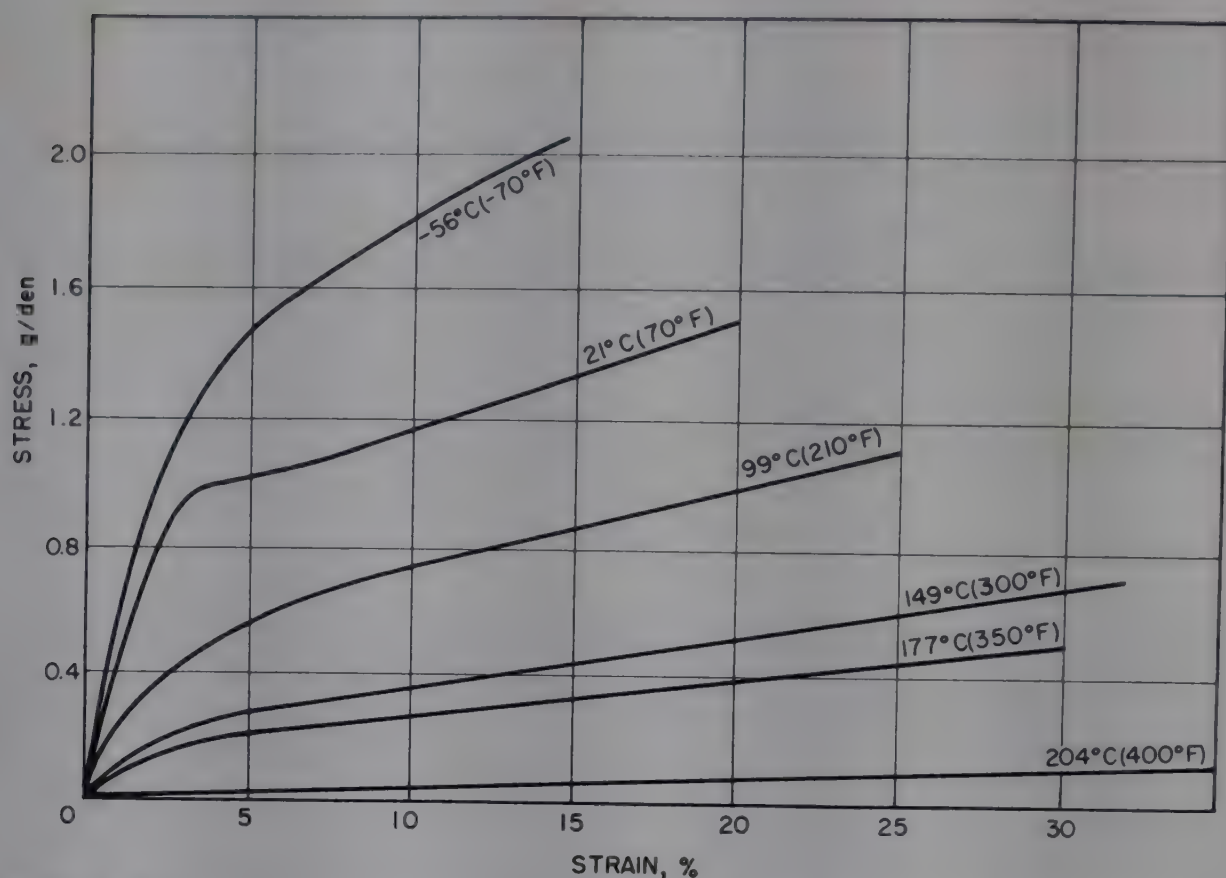


Fig. 8. Stress-strain properties of 75-den acetate yarn at various temperatures.

according to the ASTM, a figure of only 6.5% is added to the finish-free, bone-dry weight of the fiber.

Another fiber and yarn property which has become of particular importance since the advent of ease-of-care and quick-drying textiles is percent *water imbibition*. This value is determined by measuring the moisture remaining in the fiber when equilibrium is established between a fiber and air at 100% relative humidity while the fiber is being centrifuged at forces up to 1000 gravities. Average recorded values are: acetate, 24%; nonheat-treated triacetate, 16%; heat-treated triacetate, 10%.

Adsorption of water by fibers causes *swelling* which is roughly proportional to moisture content. While there is considerable disagreement among investigators in the field, the average value for the increase in length of acetate fibers due to water adsorption is about 1%; the average increase in cross section, approximately 8%. The values for the swelling of triacetate are lower than for acetate. Tesi (32) records the percent cross-sectional area increase for heat-treated Arnel triacetate at 1.5%; for the nonheat-treated fiber, at 4.0%.

Thermal Behavior. Acetate, in common with other thermoplastic fibers, will exhibit sticking, softening, and even melting when ironed, if high temperatures are used. Sticking and softening temperatures of all fibers are dependent on such factors as yarn diameter, fabric construction, and general fabric geometry, and vary with different test procedures. The sticking and softening temperatures are not necessarily related directly to the fiber melting point. Acetate softens and sticks in the range 190–205°C and fuses at approximately 260°C. The apparent shining or glazing temperature is usually lower than the sticking temperature and is also influenced by moisture content, fabric construction and color. (In the ironing of acetate fabrics, it is usually recommended that the sole-plate temperature of hand irons should not exceed 170–180°C.) The sticking and glazing temperatures of nonheat-treated triacetate are in the same range as acetate, but heat treatment of triacetate raises these

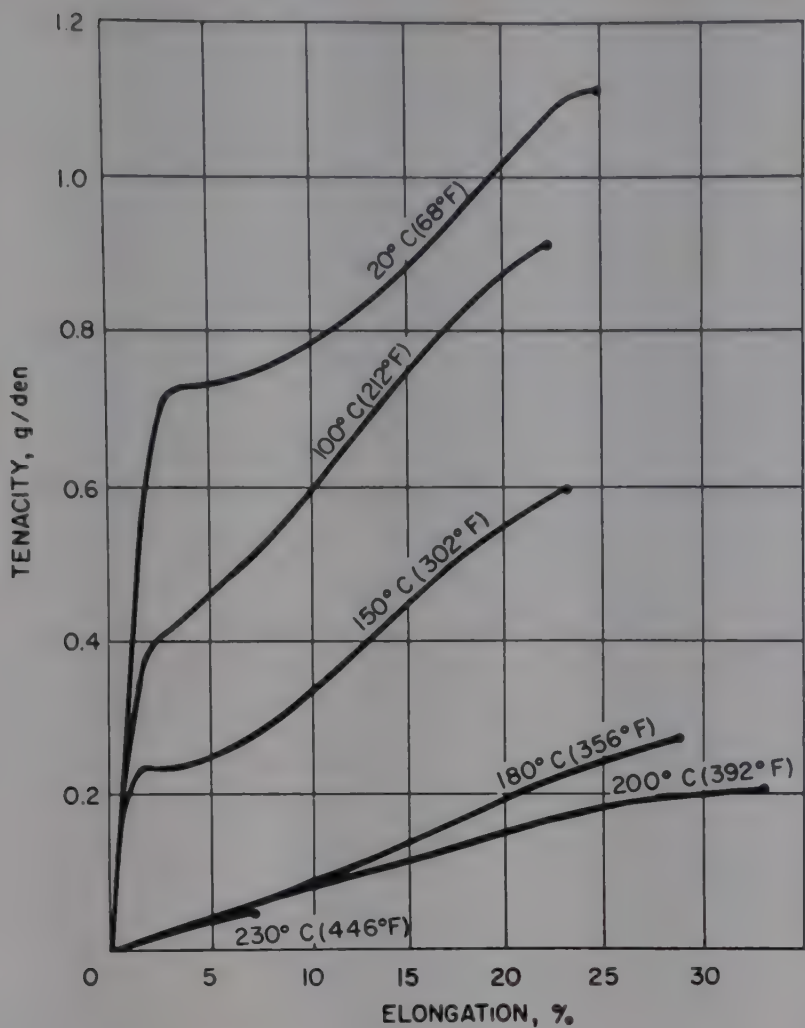


Fig. 9. Stress-strain curves of 150-den Arnel yarn.

temperatures considerably, and triacetate fabrics that were properly heat-treated can be ironed at temperatures as high as 240°C. The melting point of triacetate is 300°C.

Acetate and triacetate, being thermoplastic fibers, exhibit changes in mechanical properties as a function of temperature. However, within the range of normal climatic temperatures the mechanical properties are not altered to a significant degree. As temperature is raised, acetate and triacetate tend to elongate more readily under stress. Figure 8 shows the stress-strain curves for a typical 75-denier acetate yarn stressed at various temperatures, and illustrates the effect of temperatures on this fiber. Figure 9 illustrates the behavior of Arnel triacetate under similar conditions.

Prolonged exposure of acetate and triacetate to elevated temperatures weakens these fibers. The decrease in strength, of course, depends on the temperature and time of exposure. Table 5 shows the percent strength retained after various time

Table 5. Effect of Dry-Heat Exposure^a

Exposure, hr	Strength retained, %		
	Acetate		Triacetate
	100°C	120°C	130°C
180	95	78	88
330	91	61	80
500	84	42	70

^a Yarns tested at standard conditions (65% rh and 70°F).

intervals during which acetate yarn was exposed at 100 and 120°C. The effect on triacetate exposed at 130°C is also shown.

Light Stability. The resistance of textile fibers to sunlight degradation has been the subject of numerous studies, many of which have given not only erratic but contradictory results. This is not unexpected since many factors other than sunlight, such as humidity and atmospheric fumes, affect the rate of degradation of textile fibers. Attempts to duplicate conditions and results have been unsuccessful. Therefore, it is not possible to rate fibers accurately for their resistance to sunlight degradation in terms of Langley units or hours of exposure. Although there have been specific results which indicate that some triacetate fibers show more resistance to actinic degradation than acetate, the following generalizations appear justified at this time. Acetate and triacetate, when exposed under glass, are in the same general class as cotton and rayon; somewhat more resistant than normal pigmented nylon and silk; and appreciably less resistant than the acrylics and polyesters. When acetate and triacetate, along with other fibers, are exposed to direct weathering, their resistance is lowered as compared to exposure under glass. Additional information on actinic degradation may be found in references 33–38. Certain pigments used in solution dyeing, particularly carbon black, offer protection from Fade-Ometer-type sunlight exposure, as indicated for acetate in Table 6.

Table 6. Effect of Colored Pigments on Percent of Initial Tenacity Retained after Fade-Ometer Exposure^a

Yarn sample	Tenacity retained, %		
	100 hr	200 hr	400 hr
typical bright acetate	89.0	73.0	
typical dull acetate (TiO ₂ -pigmented)	86.0	74.5	
brown-pigmented acetate	87.5	77.6	70.5
yellow-pigmented acetate	95.8	77.6	66.6
black-pigmented acetate	100.0	95.0	93.4

^a Tenacity measured at standard conditions.

Electrical Behavior. Acetate and triacetate yarns readily develop static charges and for some purposes it is desirable to apply an antistatic finish to aid in textile processing (see Antistatic agents). Both yarns are valuable for electrical insulation. For this use, lubricants and other finishing agents are removed by solvent extraction followed by washing with water. Table 7 contains data from a report of the British Cotton Industry Association, which lists the resistance in megohms of various fibers over a range of relative humidities from 45 to 95% (40).

Although the measure of the electrical resistivity of fabrics is subject to considerable variation, the following may serve as an indication of the relative electrical resistivity of acetate and triacetate fabrics. Scoured acetate taffeta fabrics, measured according to ASTM Method D 1000-55T, gave a value of the order of 50,000 megohm per in. of width at 94–98% rh. Similar fabrics of nonheat-treated Arnel gave values of the order of 1,500,000 megohm per in. of width. Specially scoured, heat-treated fabrics of Arnel have given resistivity values of up to 400,000,000 megohm per in. of width (41). Another comparison of the electrical behavior of acetate, triacetate, and other fibers may be gleaned from Table 8, which lists dielectric strength and power factor measurements on films (41).

Table 7. Specific Electrical Resistance of Various Fibers in the Commercial and Purified States

Rh, %	Electrical resistance, megohm-cm							
	Acetate		Nylon		Cotton		Rayon	
	Com- mercial	Purified	Com- mercial	Purified	Com- mercial	Washed ^a	Com- mercial	Purified
45	967,000	81,500,000	813,000	6,430,000	149		543	1,720
50	662,000	21,600,000	585,000	3,200,000	64		235	680
55	424,000	6,040,000	387,000	1,430,000	30		95	266
60	256,000	1,650,000	208,000	525,000	14	530	36	93
65	150,000	448,000	104,000	193,000	6.0	150	13	34
70	74,000	126,000	43,000	70,000	2.4	38	4.6	12
75	28,900	33,200	14,500	20,000	1.02	11.2	1.8	4.4
80	7,200	9,000	4,000	6,000	0.33	3.1	0.63	1.5
85	1,610	2,460	863	1,290	0.106	0.91	0.23	0.52
90	160	370	120	180	0.024	0.23	0.06	0.13
95	11	39	8.5	18.5			0.012	0.02

^a Water-washed only.

Table 8. Dielectric Strengths and Power Factors of Dry Acetate, Triacetate, Orlon (Du Pont), Dacron (Du Pont), and Nylon Films

Properties	Acetate	Triacetate	Dacron polyester	Orlon acrylic	Nylon
dielectric constant, 1 megacycle/sec	5.0	3.7	3.5	4.2	3.8
power factor, 1 kilocycle/sec	0.005	0.018	0.006	0.085	0.018

Acetate and triacetate have been used as electrical insulating tapes, and tests to measure the corrosion of copper wire and strength retention of acetate and triacetate tapes have been conducted in the laboratories of Celanese Corporation. This was accomplished by interlacing copper wire through acetate and triacetate fabrics. The copper wires were placed 7 mm apart and a potential of 150–160 volts was applied. The samples were then exposed for three months at 115°C. At the end of this period, neither the copper wire nor the acetate and triacetate fabrics had lost any appreciable strength. Tests repeated at 150°C for one month showed that the copper wire was unaffected but that the acetate fabric lost about 60% of its original strength; the triacetate lost only 25%.

MECHANICAL PROPERTIES OF FIBERS AND YARNS

The mechanical properties of textile products (hand, drape, wrinkle resistance and recovery, strength and flexibility) are governed by complicated interactions of the inherent mechanical properties of the fibers and by a number of form factors. However, in dealing with specific fibers and yarns, only the inherent mechanical properties can be considered. The geometric factors change with each fabric construction and cannot be included. In regard to the mechanical properties of fibers and yarns, stress-strain and recovery behavior under conditions of tensional, bending, torsional, and shear loading will be noted.

Tensional Properties. A stress-strain typical for both commercial acetate and triacetate yarns is shown in Figure 10. Although some high-tenacity triacetates and

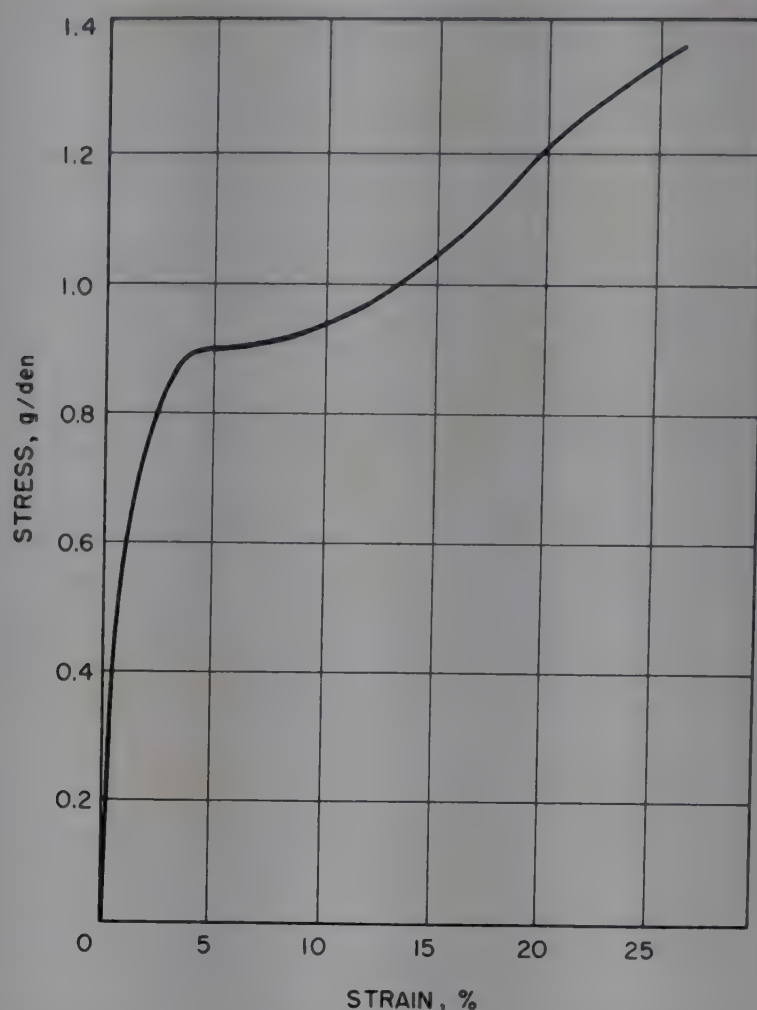


Fig. 10. Stress-strain curve typical for either an acetate or a triacetate yarn (tested on an Instron tensile tester).

acetates are being produced, this curve can well serve to characterize most commercial acetate and triacetate yarns. Table 9 shows a range of properties characteristic of both acetate and triacetate commercial yarns and fibers.

Table 9. Tenacity and Elongation of Commercial Yarns and Fibers

Properties	Acetate and triacetate
tenacity, g/den	
standard conditions	1.2-1.4
wet	0.8-1.0
knot, standard conditions	1.0-1.2
loop, standard conditions	1.0-1.2
elongation at break, %	
standard conditions	25-45
wet	35-50

The ability of a material to resist deformation under an applied tensile stress is measured by the modulus of elasticity (Young's modulus). In viscoelastic materials, the modulus is not constant since the stress-strain curve is not linear; and, accordingly, the apparent modulus of a textile fiber is here defined as the ratio of stress to strain in the initial, linear, portion of the stress-strain curve. The apparent modulus at low strain levels is directly related to many of the mechanical performance characteristics of textile end products. The modulus of elasticity can be affected by drawing (elongating) the fiber, and it is affected by other manufacturing parameters. Values for

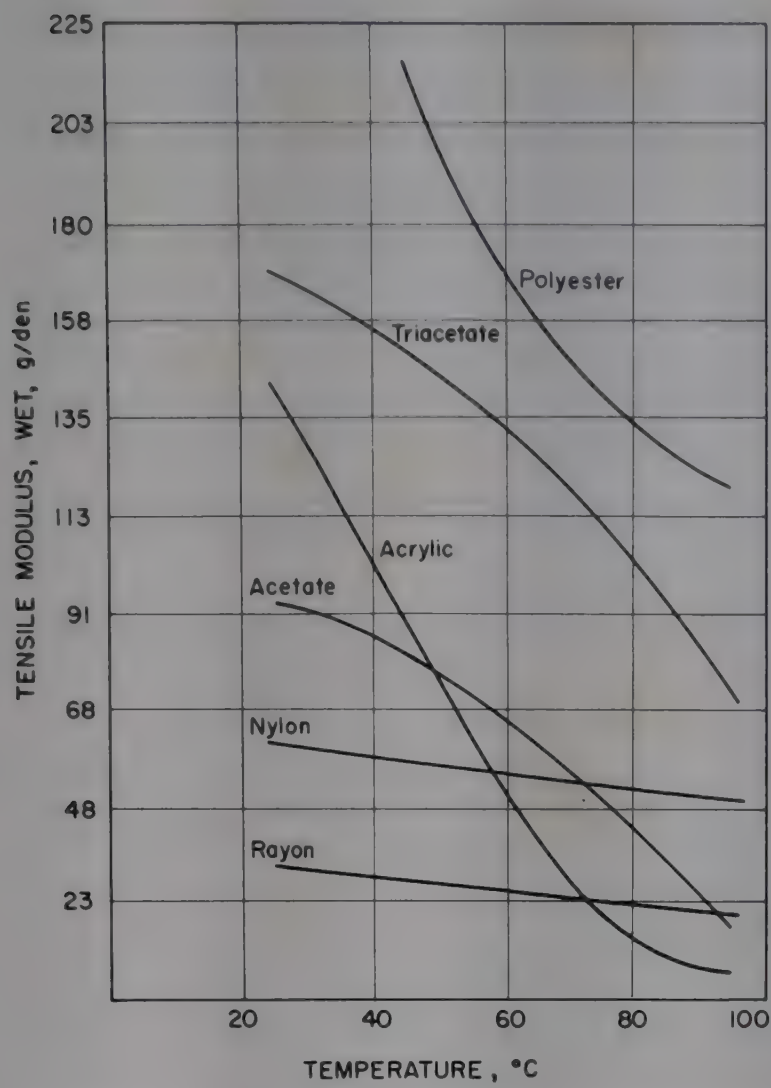


Fig. 11. Effect of water temperature on wet modulus of fibers (42).

commercial acetate and triacetate fibers are generally in the range of 22 to 48 grams per denier.

Of great significance from a textile point of view is the wet modulus of fibers at various temperatures. This is true because the wet modulus appears to have a bearing on the degree of creasing and mussiness resulting from the laundering operation. Figure 11 shows the change with temperature of the wet modulus of acetate, triacetate, and a number of other fibers (42).

The ability of a fiber to absorb energy during straining is measured by the area under its stress-strain curve. This property is also known as toughness or work of rupture. Table 10, according to Meredith (43), lists the work of rupture of acetate in comparison with other textile fibers. Work of rupture of acetate is essentially the same as of triacetate.

Table 10. Work of Rupture of Acetate and of Some Other Common Fibers

Fibers	Work (toughness), g-cm/(cm-den)
acetate	0.25
cotton	0.11
nylon	0.86
rayon (viscose regular)	0.26
silk	0.82
wool	0.36

A measure of the elastic recovery of acetate and triacetate compared to polyesters and acrylics can be obtained from Table 11. This table shows the percent tensile strain recovery when the fibers are stressed at two different rates up to 5 and 10% elongation.

Table 11. Tensile-Strain^a Recovery, %

Elongation	Acetate	Triacetate	Acrylic	Polyester
from 5% elongation				
at 10%/min	60	60	68	69
at 60%/min	60	70	78	82
from 10% elongation				
at 10%/min	34	30	52	42
at 60%/min	30	40	56	58

^a Strain level of 5 and 10%, held for one minute; stress removed and fiber measured for recovery after three minutes.

A fiber which is strained and then allowed to recover will give up a portion of the work absorbed during straining. The ratio of the work recovered to the total work absorbed (measured by the respective areas under the stress-strain and stress-recovery curves) is designated as resilience.

Bending. The bending properties of a fiber are in general dependent on the viscoelastic behavior of the material. However, in most normal textile applications the radius of curvature of bending is relatively great and the imposed strains are, accordingly, of a low order of magnitude. Therefore, as a first approximation, it is possible to examine the bending properties by the classical methods. The bending stiffness, or flexural rigidity, of a fiber is the product of the bending modulus and the moment of inertia of the cross section. Thus, for fibers of round cross section and constant modulus, the flexural rigidity will vary directly with the square of the denier. Table 12 gives data on the flexural rigidity of acetate fibers as a function of fiber denier.

Table 12. Flexural Rigidity of Acetate Fibers as a Function of Denier

Fiber denier	Flex rigidity, g-cm ²
60	0.0083
30	0.0027
20	0.0089
15	0.0074
10	0.0025
5	0.0056
3.75	0.0035

Torsion and Shear. There is a dearth of specific data concerning torsional and shear properties of acetate and other fibers. (For a discussion of these topics, see reference 44.)

CHEMICAL PROPERTIES

In slightly acid or basic conditions and at room temperature, acetate and triacetate are very resistant to chlorine bleach at the concentrations normally encountered in laundering. This is illustrated by the result of a test wherein knitted fabrics were

washed and tumble-dried up to 100 cycles using 200 ppm of chlorine in the wash water (41). After 100 cycles, the Arnel triacetate and the acetate fabrics retained essentially 100% of their strength. Whereas similar fabrics knitted from nylon retained 15%, rayon fabrics were completely destroyed after 65 cycles.

Triacetate is significantly more resistant than acetate to alkalis of the type encountered in normal textile operations. In the dyeing of acetate, it is recommended that temperatures no higher than 85°C and a pH below 9.5 be used. Otherwise, delustering may take place. But triacetate, under normal scouring and dyeing conditions, permits the use of alkalis up to pH 9.5 and of temperatures up to 96°F, with

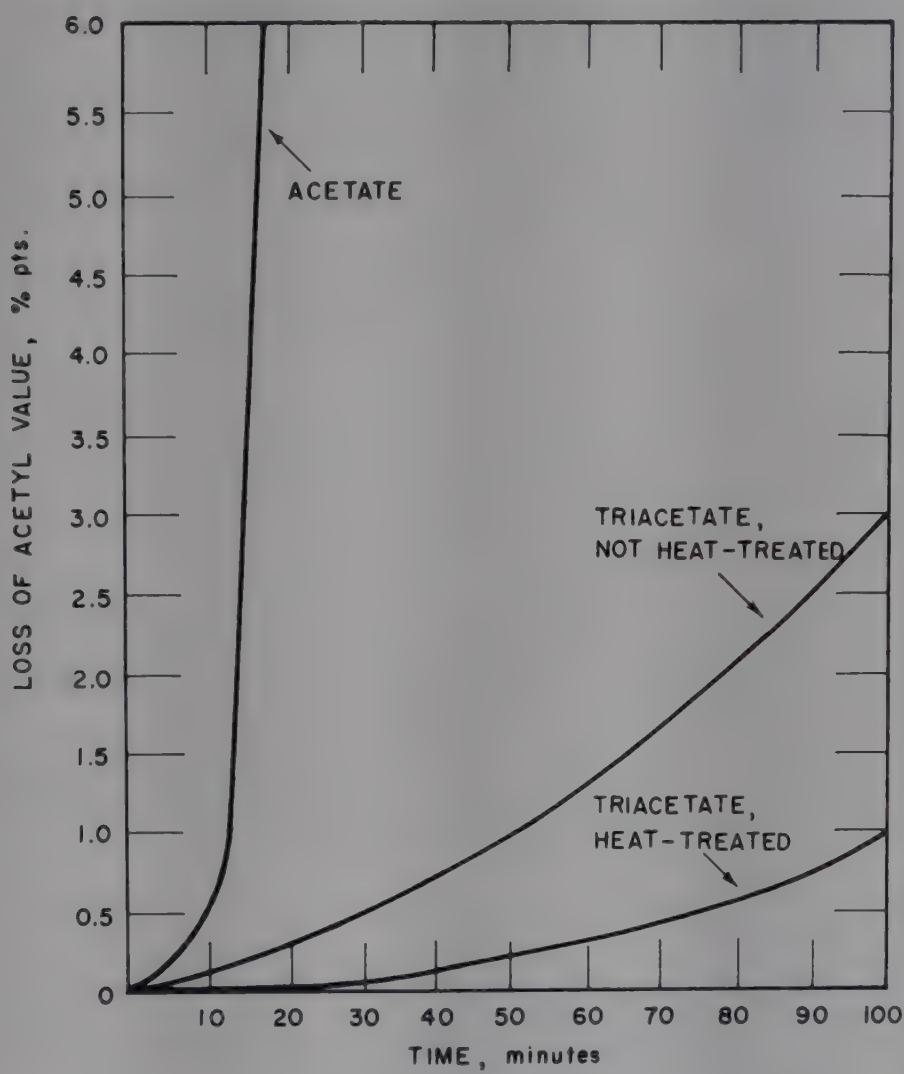


Fig. 12. Results of alkali treatment. Comparative saponification rates of acetate vs Arnel triacetate. (Temperature 50°C, caustic soda concentration 11 g/l.)

little saponification or delustering. Heat-treated triacetate has even greater alkali resistance, as shown in Figure 12. Strong alkalis and boiling temperatures will saponify and deluster triacetate as well as acetate.

Acetate and triacetate are unaffected by dilute solutions of weak acids. Strong mineral acids cause serious degradation of both fibers. Reference 41 lists the results of exposure of Arnel triacetate to various acids, and reference 45 shows the effect of a number of acids on acetate yarns.

Acetate and triacetate are unaffected by the drycleaning solutions normally used in the U.S.A. and Canada. Trichloroethylene, used to a limited extent in Great Britain and Europe, softens triacetate.

RESISTANCE TO MICROORGANISMS AND INSECTS

The resistance (based on soil acid tests) of triacetate to microorganisms is very high, approaching that of polyester, acrylics, and nylon. Figure 13 shows comparative soil-burial test results on acetate, triacetate, and cotton. Neither acetate nor triacetate is readily attacked by moths or carpet beetles. However, there have been a few instances where these larvae have cut through acetate to get at wool fibers, or have damaged acetate that was contaminated with foreign substances containing starches. If ingested by humans, both acetate and triacetate will remain undigested and cause no harmful reactions. No cases of toxic effects, skin irritations, or allergic reactions attributable to acetate or triacetate fibers have been reported.

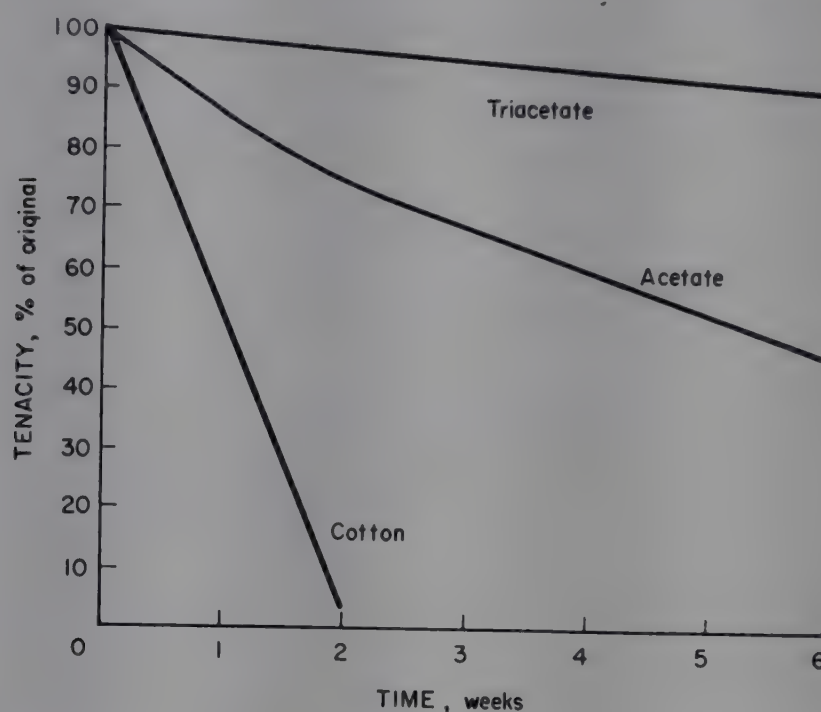


Fig. 13. Resistance to biological attack as measured by residual tenacity after various periods of soil burial.

Dyeing

Of the various classes of dyes commercially available for dyeing acetate and triacetate (namely, acid, metalized acid, basic, disperse, direct, naphthols, and vats), disperse dyes are used to the greatest extent. Naphthols and acetate dyes in solvents have been used where special fastness requirements were essential. (See Dyes, application; also references 30, 46-53.)

The action of the disperse class of dyes in the dyeing of acetate and triacetate is also described in the references listed above. Unlike the direct dyes for rayon and cotton, and unlike the acid dyes for wool and nylon, the disperse dyes are nonionic, have a relatively low solubility even under high-temperature dyeing conditions, and are high-melting, crystalline materials. For the effective dyeing of acetate and triacetate, and to prevent agglomeration during dyeing, this class of dyes must be milled to a very small particle size and must then be dispersed effectively. Dyeing with this class of dyes proceeds by (1) solution of a small fraction of disperse dye in the aqueous medium; (2) diffusion of the individual, dissolved molecules of dye to the fiber surface; and (3) absorption and diffusion of the individual dye molecules throughout the fiber cross section.

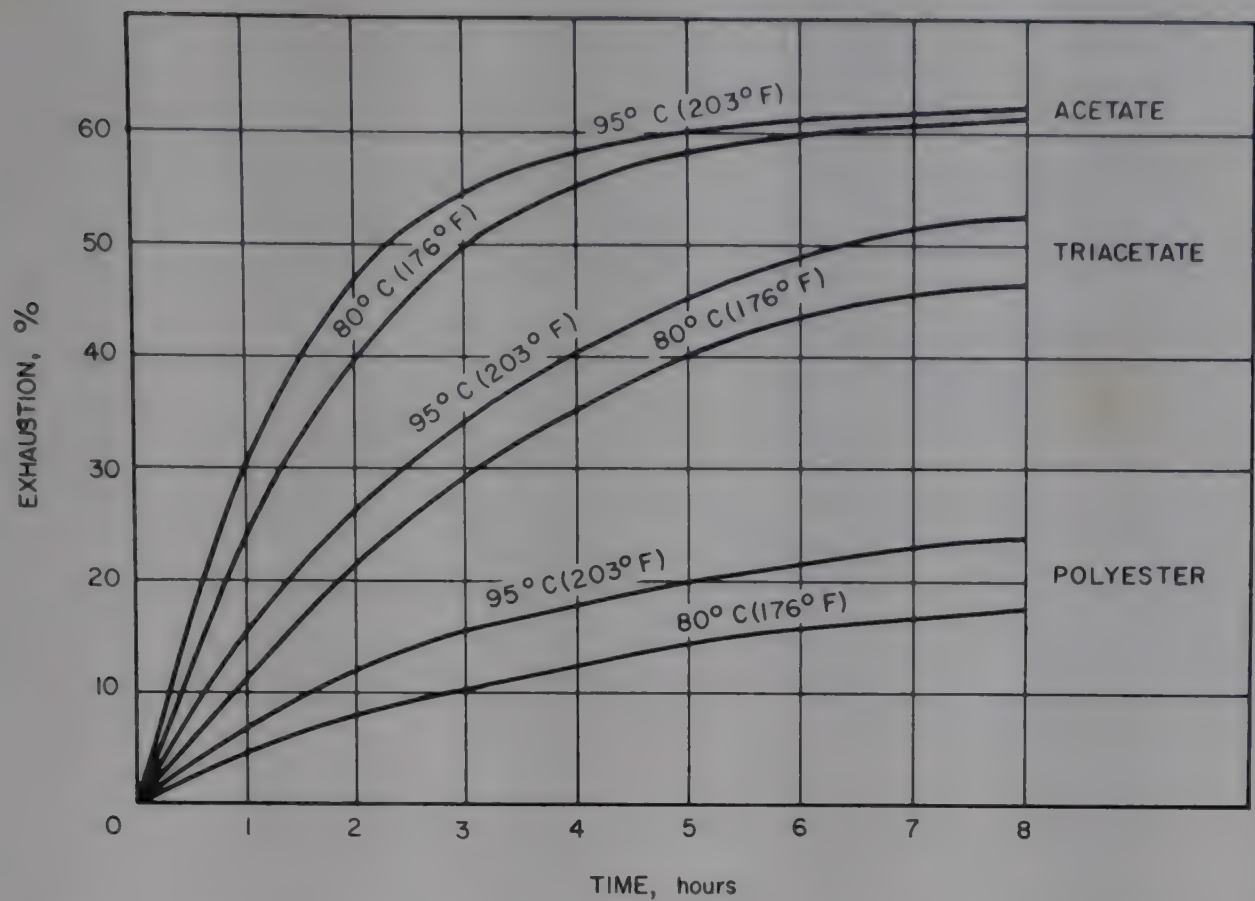


Fig. 14. Relative dyeing rates of acetate, Arnel triacetate, and Dacron polyester with 2% Lenra Blue RLS at 50:1 liquor ratio.

Under normal dyeing conditions, the rate-determining step in the dyeing of acetate and triacetate is diffusion of the relatively large dye molecules in the fiber. The effects of the nature of fiber composition and the influence of temperature are illustrated in Figure 14 (51). As can be seen, triacetate fibers dye at a significantly slower rate than acetate, even at 95°C. In commercial dyeing, the rate of dyeing triacetate is greatly accelerated by the addition of emulsions of *o*-phenylphenol or butyl benzoate to the dyebath.

Optimum colorfastness on dyed acetate and triacetate fabrics can only be achieved by careful selection from among thousands of azo, anthraquinone, and diphenylamine disperse dyes which are available. Heat treatment of dyed triacetate fabrics has the multiple purpose of raising the safe ironing point, improving colorfastness to washing, and achieving greater resistance to gas fading by driving the dye further into the fiber.

Solution-Dyed Yarns. About 50 to 60% of acetate and triacetate production contains small quantities—usually less than 1.5%—of TiO₂ as a delustrant. The remainder, usually designated as “bright” yarn, contains no added pigments.

Acetate, and, to a limited extent, triacetate are being produced in solution-dyed colors. This method of coloration is accomplished by adding suitable coloring agents, usually organic or inorganic pigments, to the spinning dope prior to extrusion; it is sometimes referred to as “dope dyeing.”

In Europe, where the dyeing of acetate and triacetate is relatively more expensive than in the U.S.A., extensive use is made of soluble dyes instead of pigments in the solution-dyeing process. These solvent-soluble dyes offer the advantage of low cost and easier handling since they do not have to be dispersed in the acetate or triacetate before use.

Three processes may be used to incorporate the coloring agents into the spinning solution. They are (1) *mass dope coloration*, in which the complete batch of spinning dope is thoroughly blended with the color dispersion; (2) *the high-concentration injection method*, which involves the injection, prior to extrusion, of high color concentrates into the dope with mixing and pressure; and (3) *the direction injection method*, whereby the prepared color is injected into the dope at the spinnerets. In all three methods the yarn thus emerges already colored and can be used in "loom finished" fabrics, a term indicating that fabrics are finished as they "come off the loom," thus requiring no wet processing in dyeing establishments.

In the U.S.A. the two major producers of solution-dyed acetate yarns—Celanese Fibers Company and Tennessee Eastman—offer about thirty colors each, ranging from light pastel pink and yellow to dark navy and black. When suitable coloring components are used, these solution-dyed yarns provide the maximum in colorfastness properties (for a list of some of the colorants used for acetate yarns, see ref. 54). There are no commercial quantities of acetate or triacetate solution-dyed staple being produced in this country.

Uses

Acetate filament yarns and staple fibers are used in essentially all types of wearing apparel. The most important are dresses, blouses, lingerie, bathing suits, linings, ribbons, neckties, men's and women's sportswear, hat bands, underwear, dressing gowns, and bathing interlinings. The household textile field uses acetate extensively in curtains, drapes, upholstery, slip covers, and fillings for pillows and furniture. Important industrial applications for acetate are electrical insulation, liquid filters, air filters, and filters for cigarettes. The amount of acetate tow used for cigaret filters increased from 0.7 million pounds in 1951 to 93.1 million in 1960 (55).

Triacetate finds application in many of the same fields as acetate but in addition is particularly suitable where ease-of-care and durably pleated garments are desired. Among the most important apparel uses for triacetate are pleated skirts, men's and women's slacks, men's summer jackets and tropical suits, casual and sport shirts. Industrial uses include laundry pads, press cloths, wire covering, and dust collector bags.

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ACETIC ACID, CH_3COOH . See Ethanoic acid.

ACETIC ACID DERIVATIVES

Acetyl chloride.....	138
Acetamide.....	142
Dimethylacetamide.....	145
Acetanilide.....	148

For chloro-, bromo-, and iodoacetic acids see Ethanoic acid. For fluorine derivatives, see Fluorine compounds, organic.

Acetyl Chloride

Acetyl chloride (ethanoyl chloride), CH_3COCl (abbreviated as AcCl), molecular weight 78.501, is sold as a colorless, flammable, mobile liquid which fumes in moist air. It has a pungent odor and its vapors are extremely irritating to the eyes, nose, and throat. Concentrations in air of 1 ppm or even lower are readily detectable by a lacrimatory effect. Acetyl chloride is easily hydrolyzed into acetic acid and hydrochloric acid by body moisture (25). It also has a toxic effect of its own because it reacts with the SH group of protein molecules (26).

Physical and Chemical Properties. Fp, -112.86°C ; bp, 51.8°C ; flash pt, 4.5°C ; vapor pressure at -19.5 – 49.0°C , $\log P_{\text{mm}} = (-3570.87/T) + 1.75 \log T - 0.02367T + 17.16999$ (see also ref. 27); d_4^{20} , 1.1051; vapor density (air = 1), 2.70; n_D^{20} , 1.38708; surface tension, 26.7 ± 1.0 dynes/cm at 14.8°C , and 21.9 dynes/

cm at 46.2°C; specific heat, $1.419 \pm 1\%$ joules/g; heat of vaporization, 87.14 cal/g at 50.4°C; heat of combustion of the vapor (constant volume), 242.0 kcal/gram-mole; viscosity data, see ref. 2; latent heat of fusion ΔH_f (liquid), 65.8 kcal/mole; bond dissociation energy of carbon-chlorine bond, 76.7 kcal; mass spectrum at 75 ev, see ref. 28; Raman spectrum, see refs. 29 and 30; infrared spectrum, see ref. 31; UV spectrum in ethyl ether solution, see ref. 32. Electron diffraction determinations (33) of the molecular structure of acetyl chloride in the vapor state have shown the following lengths for bonds: carbon-oxygen, 1.22 ± 0.04 Å; carbon-carbon, 1.50 ± 0.04 Å; and carbon-chlorine, 1.77 ± 0.02 Å. Acetyl chloride is soluble in acetone, glacial acetic acid, ethyl ether, benzene, toluene, chloroform, and carbon disulfide.

Acetyl chloride decomposes vigorously in water to form acetic acid and hydrochloric acid. Its hydrolysis rate in acetone-water solutions is first order with respect to water and acetyl chloride over the range studied (34). Acetyl chloride reacts with primary and secondary alcohols to produce the corresponding esters and hydrogen chloride; its reaction with tertiary alcohols yields the tertiary alkyl chloride and acetic acid. Acetyl chloride reacts with primary and secondary amines to give their corresponding acetyl derivatives, but tertiary amines form addition compounds (3). Thus, acetamide is formed by treating acetyl chloride with anhydrous ammonia or with concentrated aqueous ammoniacal solutions; aniline reacts to give acetanilide.

Potassium sulfide and potassium hydrogen sulfide react with acetyl chloride to form acetyl sulfide and thioacetic acid, respectively. Acetyl chloride reacts with acetylene at 15°C in the presence of aluminum chloride to give a 70% yield (based on AcCl) of β -chlorovinyl methyl ketone, $\text{CH}_3\text{COCH}=\text{CHCl}$ (35); with aluminum chloride, under the same conditions, it gives methyl vinyl ketone and hydrogen chloride. Monovinyl acetylene and acetyl chloride, in the presence of water and cuprous chloride, give a 75–80% yield of chloroprene (36). Acetic anhydride is formed in the reaction of acetyl chloride with sodium acetate. Unsymmetrical anhydrides are formed when acetyl chloride reacts with other carboxylic acids or their salts. Hydrocyanic acid reacts with acetyl chloride to produce acetyl cyanide; the latter, in the presence of concentrated hydrochloric acid, forms the pyruvic acid amide $\text{CH}_3\text{COCONH}_2$. 2-Hexanone can be made, in 75% yield, by causing acetyl chloride to react with butylmagnesium chloride (4).

Acetyl chloride decomposes at 400°C, over a nickel catalyst, into carbon monoxide (62%), hydrogen (32%), hydrogen chloride, ethylene, and carbon dioxide. It reacts with zinc (5), aluminum, and other metals (6) to form the chloride of the metal and a variety of organic compounds. The corrosiveness of acetyl chloride to most of the commonly used industrial metals (especially if water is present) has limited its use in industry. Monel, nickel, and lead, however, have a fair resistance (37). In the presence of a trace of iodine, acetyl chloride reacts with chlorine to form chloroacetyl chloride (a reaction also catalyzed by sunlight). This reaction, under more severe conditions, occurs also in the absence of iodine (38), and is an intermediate step in several processes for the chlorination of acetic acid. Acetyl chloride also reacts with bromine to give a mixture of bromoacetyl bromide and bromoacetyl chloride; with hydrogen bromide (or potassium bromide) to produce acetyl bromide; with calcium iodide or hydriodic acid to form acetyl iodide; and with zinc fluoride, or potassium fluoride in acetic acid solution, to form acetyl fluoride. Acetyl chloride forms additional complexes when reacted with aluminum chloride or ferric chloride. In the presence of a Friedel-Crafts catalyst, such as aluminum chloride, many aromatic

compounds may be acetylated by means of acetyl chloride; eg, benzene to acetophenone (39); benzene + cyclohexene to 4-phenylhexahydroacetophenone (40); and naphthalene to a mixture of 1- and 2-acetonaphthone (41).

Preparation and Manufacture. Acetyl chloride has been prepared by the action of various chlorinating agents on acetic acid, its salts, esters, or anhydride. It is conveniently prepared by treating acetic anhydride with hydrogen chloride at 85–90°C; the yield is practically quantitative (7). This method is used industrially on a large scale for the in situ production of acetyl chloride as a catalyst for the chlorination of acetic acid; it is also easily adaptable to the large-scale production of high-purity acetyl chloride (42), by fractional distillation of the reaction product. The usual laboratory method involves the slow addition, with initial cooling, of phosphorus trichloride to acetic acid; the mixture is then warmed to 40–50°C to expel gaseous hydrogen chloride, and the acetyl chloride is distilled from the lower layer of phosphorous acid; repeated distillation leads to pure acetyl chloride (8).

An 85% yield of acetyl chloride is obtained by heating benzoyl chloride with acetic acid in a 2:1 molar ratio (9). In the presence of a catalyst, such as zinc chloride or sulfuric acid, benzotrichloride reacts with acetic acid to form acetyl chloride and benzoyl chloride (10,11). Acetic acid in the liquid or vapor phase reacts with phosgene to give acetyl chloride (12,13). Another method involves the chlorination of glacial acetic acid, in the presence of phosphorus trichloride at 10–30°C (14). It is also formed by causing methyl chloride to react, at elevated temperatures, with carbon monoxide in the presence of boric acid, copper (15), phosphoric acid, or the salts of these acids. If carbon monoxide and methyl chloride are passed above 600°C through a vessel having a smooth, heat-resistant, nonmetallic surface, acetyl chloride can be made in >90% yield without a catalyst (43). In the presence of a catalyst, such as activated carbon or aluminum chloride, ketene reacts with anhydrous hydrogen chloride to give acetyl chloride. When a mixture of calcium chloride and acetic anhydride (containing borontrifluoride etherate) is heated at 180–200°C and then distilled, an 80% yield (based on calcium chloride) of acetyl chloride is obtained (17). Similarly, acetic acid reacts with carbon tetrachloride and copper tungstate catalyst, at 200°C, under autogenous pressure, to give 15% acetyl chloride (18). The chlorination of acetaldehyde, in a tile-lined tower, produces acetyl chloride (19). Acetyl chloride containing C¹⁴ in the α position has been prepared by using BaC¹⁴O₃ as the starting material (20).

Commercially, acetyl chloride is prepared by treating sulfur dioxide and chlorine with sodium acetate (preferably with cooling), followed by distillation (21).

Acetyl chloride is shipped in 13-gal (150-lb) glass carboys and in 4-oz and 1-lb packages. Industrial equipment for acetyl chloride is usually made of glass, glass-lined steel, impervious impregnated graphite, porcelain, or chemical stoneware. Of the plastics, polytetrafluoroethylene is totally resistant and is the preferred gasket material for acetyl chloride; several other plastics, including polyethylene, polypropylene, Penton, and black-filled neoprene are sufficiently resistant under certain conditions.

Uses and Applications. Acetyl chloride is used on a large scale as a catalyst in the chlorination of acetic acid; for this purpose, it is usually made in situ from acetic anhydride and by-product hydrogen chloride from the chlorination reaction. Acetyl chloride is a powerful acetylating agent, especially when used with an aluminum chloride catalyst, and will acetylate many compounds (eg, benzene) which cannot be

acetylated with acetic acid or acetic anhydride; it is therefore often used for introducing the acetyl group in complex organic syntheses. Acetyl chloride is also employed in the preparation of acetanilide, acetophenone, and other industrial acetyl derivatives, including anhydrides of carboxylic acids.

An important laboratory use of acetyl chloride is in the determination of hydroxyl groups (22), in qualitative organic analyses for distinguishing tertiary amines from primary and secondary amines and for forming derivatives of phenolic compounds. It sometimes serves as a convenient means for removing water or for saturating an aqueous solution with hydrochloric acid (23), and as a chlorinating agent for inorganic compounds. Acetyl chloride has been used as a catalyst in the esterification and halogenation of aliphatic acids and in the nitration of thiophenes and other compounds. Recently, acetyl acetone has been prepared in 80% yield from acetyl chloride by a three-stage process involving an addition compound of acetyl chloride and aluminum chloride (24).

Patents have also been granted for the use of acetyl chloride (1) as a catalyst in the esterification of cellulose (44) by acetic anhydride, to accelerate the reaction and improve the wetfastness of the resultant yarns; (2) in the manufacture of a pour-point depressant (45) for lubricating grease; and (3) as a stabilizer (46) against polymerization of organic isocyanates or diisocyanates.

In spite of its many uses, acetyl chloride has not been widely sold, probably because of the difficulty in shipping so corrosive a chemical. For larger-volume uses, it is made most conveniently either in situ or as required in another unit of the same plant. Thus recent U.S. sales figures are not available. Quoted price, in glass containers, is about 80¢/lb, although acetyl chloride is potentially a very cheap chemical if made in large volume.

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Acetamide

Acetamide (acetic acid amide, ethanamide), CH_3CONH_2 , mol wt 59.07, is the amido derivative (see Amides, acid) of acetic acid. It is commercially available as white to slightly yellow deliquescent crystals. When pure, it is odorless; frequently it has a mousy odor attributed to an unknown impurity. Acetamide is characterized chiefly by its remarkable solvent powers. It is linked to hydrocarbons through its methyl groups; to ketones, esters, and acids through its carbonyl group; to alcohol and water through its tautomeric hydroxyl group, $\text{CH}_3\text{C}(\text{OH})=\text{NH}$; and to ammonia, ammonium salts, and ammonia derivatives through its amino group. Furthermore, its high dielectric constant enhances its solvent action on inorganic compounds (2). No significant hazards are involved in the normal handling and use

of this product. Because of its deliquescent properties it should be stored in a cool, dry area.

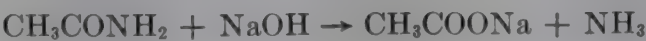
Physical Properties. Mp, 81.0°C; bp, 221.2°C; vapor pressure at 105°C, 10.0 mm Hg; $n_D^{78.3}$, 1.4274; d_{20}^{20} , 1.159; latent heat of fusion, 60.13 cal/g. On crystallization, acetamide may form a metastable crystal melting as low as 69°C, which changes slowly to the stable form on standing but changes rapidly on seeding with a crystal of the stable form. This change is accompanied by an evolution of heat. The solubility of acetamide in water and in alcohol is given in Table 1.

Table 1. Solubility of Acetamide

Temperature, °C	Moles acetamide/100 moles soln		Temperature, °C	Moles acetamide/100 moles soln	
	in water	in ethyl alcohol		in water	in ethyl alcohol
0	29.6	18.5	40	55.5	53.5
10	34.0	26.0	50	64.0	64.5
20	40.8	33.8	60	74.0	76.5
30	47.7	43.0			

In 1933, the solubility of some four-hundred compounds in acetamide was investigated (2). It was found that among the organic compounds, sixty-five ammonia-nitrogen derivatives (except uric acid), seventeen carbohydrates (except cellulose but including starch), sixty-eight dyes, forty-four alcohols, eleven nitro and nitroso compounds, and a number of miscellaneous nitrogen derivatives all dissolve readily. Of the twenty hydrocarbons tested, anthracene, phenanthrene, and triphenylmethane are quite soluble; the others are soluble at higher temperatures but form two-phase systems at lower temperatures (80–120°C). All of the forty-five acids tested dissolved. Twenty oxygen-containing compounds are soluble; ethers appear slightly less soluble than the others of this category.

Chemical Properties. Acetamide is generally regarded as a neutral substance whose acidic and basic properties are so weak that they are not manifested in aqueous solution. However, unstable salts are formed with hydrogen halides; alkali metals react to give the corresponding metal derivative, ie, CH₃CONHNa. In the cold, chlorine or bromine react with acetamide to form the corresponding *N*-halogenated amides, CH₃CONHCl or CH₃CONHBr; these compounds can be used as special halogenating agents. Acetamide is saponified by hot alkali and hydrolyzed by hot acid according to the equations



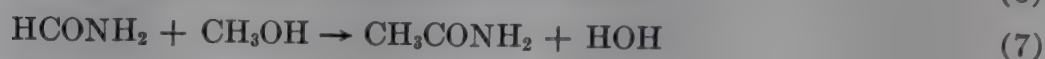
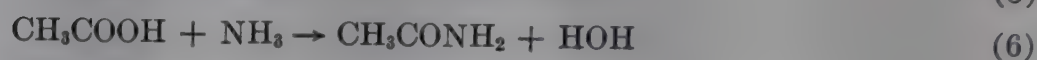
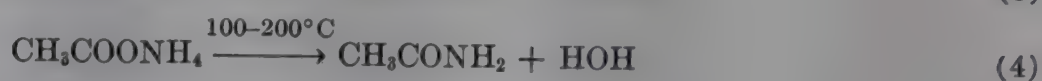
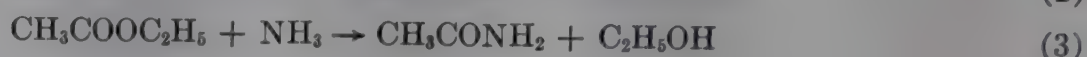
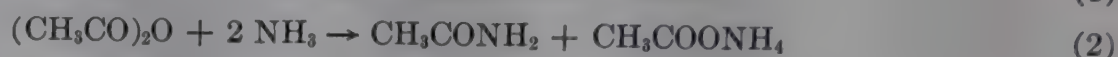
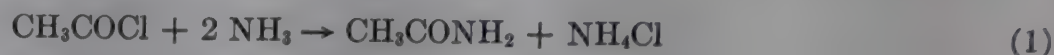
It is converted to acetic acid by reaction with nitrous acid. Acetamide also undergoes the Hofmann reaction to yield monomethylamine, according to the equations



When distilled in the presence of phosphorus pentoxide, acetamide is converted to acetonitrile, CH₃CN. The latter is also obtained by heating acetamide, at 98°C, with acetic anhydride; an 83% conversion is obtained.

Acetamide reacts with ketene or acetyl bromide to produce acetoacetamide, $\text{CH}_3\text{CONHCOCH}_3$, in better than 50% yield. It is oxidized by sulfuric acid, at 300°C , to sulfur dioxide and carbon monoxide.

Manufacture and Preparation. Acetamide may be prepared in several ways, the most important of which are as follows:



The most efficient commercial method of manufacture is by the distillation of ammonium acetate (eq. 4). Acetamide is usually made by a batch process in a glass-lined unit with a capacity of about 500 gal. This unit is charged with acetic acid and ammonia, and heated under reflux for several hours. The unreacted acetic acid, ammonia, and ammonium acetate are removed and are used in subsequent batches. The remaining acetamide is either purified by distillation or is run into pans in which it is crystallized. The crystals are centrifuged and washed. The chemically pure (cp) material is made by further recrystallization. Acetamide is produced in a technical grade and in a chemically pure, odorless grade; these have the specifications given in Table 2.

Table 2. Specifications for Acetamide^a

Specification	Technical	Cp odorless	Specification	Technical	Cp odorless
acetamide, %	99 min	99.5-99.9	color	grayish	white
free acid			odor	slight	none
(acetic), %	0.3 max	trace	melting		
chlorides	none	none	point, $^\circ\text{C}$	77-79	79-81
sulfates	none	none	nonvolatile, %		0.04 max

^a Courtesy Niacet Chemicals Division, U.S. Vanadium Corporation (from Bulletin No. 2).

Acetamide is detected by hydrolyzing it to the acid or ester. A convenient derivative for its identification is obtained by having phthaloyl chloride act on acetamide to yield *N*-acetylphthalimide.

Uses. The outstanding properties of acetamide as a solvent for most organic and inorganic compounds have led to its widespread industrial use in this capacity. Special applications are in cryoscopy, in soldering (as a flux ingredient), in the textile industry (as a dye solvent and assistant), and in urea molding compounds. The neutral and amphoteric characteristics of acetamide make it valuable as an antacid in the lacquer, explosives, and cosmetics industries. Its hygroscopic properties are the reason for its use as a plasticizer in leather, cloth, and various films and coatings, and as a humectant for paper. Miscellaneous applications also include its use as an activator in bleach liquors, as a wetting agent and penetration accelerator in dyeing, as a

special food for promoting mold growths, and as a raw material in organic syntheses, especially of methylamine and medicinals. Acetamide is also employed in the manufacture of thioacetamide and a variety of plastics. In addition, it has been used in the preparation of hypnotics and insecticides.

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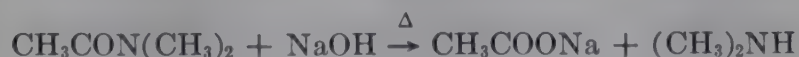
Dimethylacetamide

Dimethylacetamide (DMAC), $\text{CH}_3\text{CON}(\text{CH}_3)_2$, molecular weight 87.12, is a colorless, high-boiling polar solvent. It has good dissolving power for a wide range of organic and inorganic compounds, and is completely miscible with water, ethers, esters, ketones, and aromatic compounds. Unsaturated aliphatics are highly soluble, but saturated aliphatics have limited solubility in DMAC. Dimethylacetamide is capable of converting molecules into reactive forms by solvation and by its high dielectric effect. It has the unusual ability to serve as a solvent and reaction catalyst, often producing higher yields of purer product in a shorter time.

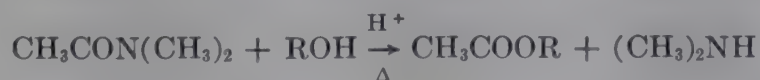
The rate of hydrolysis of DMAC is very low but increases somewhat in the presence of acids or bases. The greater stability of DMAC enables it to be recovered by distillation more economically than other similar solvents. In the absence of water, acids, or bases, DMAC is stable at room temperatures up to its atmospheric boiling point.

Chemical Reactions. The chemical reactions of DMAC are typical of those of disubstituted amides. Under suitable conditions DMAC will react as follows:

1. Saponification in the presence of strong bases and heat.



2. Alcoholysis in the presence of hydrogen ions and heat.

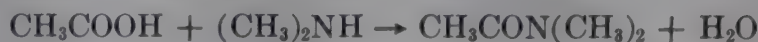


Physical Properties. Bp, 165.5°C; fp, -20°C; vapor pressure at 25°C, 1.3 mm; sp gr at 15.5/4°C, 0.9448; viscosity at 25°C, 0.92 cp; refractive index, n_D^{25} , 1.4356; dielectric constant, 37.8; dipole moment (in dioxane), 3.79; flash pt (Tag open cup), 70°C; thermal conductivity at 22.2°C, 416×10^{-6} cal/(sec)(cm²)(°C/cm); heat of vaporization at 165°C (calcd), 10,360 cal/mole; sp heat, 0.873 cal/(°C)(g); heat of combustion 608 kcal/gram-mole; DMAC-acetic acid azeotrope (84.1 and 15.9 wt %, respectively) at 170.8°C and 760 mm.

MANUFACTURE

Dimethylacetamide can be produced in the following ways:

1. By the reaction of acetic acid and dimethylamine,



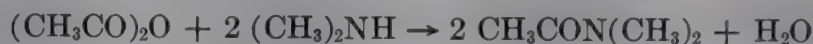
The product of this reaction can be removed as an azeotrope (84.1% amide, 15.9% acetic acid) which boils at 170.8–170.9°C. Acid present in the azeotrope can be removed by the addition of solid caustic soda followed by distillation (1).

In another procedure, the DMAC–acetic acid azeotrope is recycled to the reactor.

The reaction can also take place in a solution with a DMAC/acetic acid ratio higher than the azeotropic composition, so that an azeotrope is not formed. To this end, dimethylamine is added somewhat in excess over the exact stoichiometric proportion of acetic acid (2).

If a substantial excess of dimethylamine is reacted with acetic acid under conditions of elevated temperature and pressure, a reduced amount of azeotrope is formed. Optimum temperatures are between 250 and 325°C, and pressures in excess of 900 psi are required (3).

2. By the reaction of acetic anhydride and dimethylamine,



Dimethylamine is added somewhat in excess of the stoichiometric proportion of acetic acid (2).

USES

The uses for dimethylacetamide are very similar to those for dimethylformamide (DMF) (see Formic Acid). Although DMAC is employed less often than DMF because of its relatively recent commercial availability, its uses and its production are increasing, and its price is approaching that of DMF.

Solvent for Polymers. Dimethylacetamide (DMAC) is an excellent solvent for synthetic and natural resins. It readily dissolves vinyls, acrylates, cellulose derivatives, styrenes, and linear polyesters.

A major use is as a spinning solvent in the production of acrylic fibers. DMAC has been found useful as a solvent not only for polyacrylonitrile, but also for its copolymers and interpolymers. Copolymers containing at least 85% acrylonitrile can be dissolved in DMAC to form solutions suitable for the production of films and yarns (4,5). DMAC is claimed as an excellent solvent for the copolymers of acrylonitrile with vinyl formate (6), vinylpyridine (7), and allyl glycidyl ether (8).

At elevated temperatures, polymers containing over 50% vinylidene chloride are soluble up to 20% in DMAC, and such solutions are useful in the preparation of fibers and films (9).

As a solvent for high-molecular-weight poly(vinyl chloride), DMAC forms a synergistic mixture with tetrahydrofuran (10).

Catalyst and Solvent for Reactions. Dimethylacetamide is used by the pharmaceutical industry as a reaction solvent. Numerous cases of the use of DMAC as a reaction catalyst and solvent are given in the literature. A few will be cited to illustrate the types of reactions improved by the use of DMAC. The dehydrobromination of steroids may be carried out readily with lithium chloride in DMAC (11). The chlorination of alkyl methacrylates to give lower alkyl esters of 2,3-dichloroisobutyric

acid is catalyzed by amides, such as DMAC, which are included in the reaction mixture in concentrations of 1 to 10% (12).

Cyanuric acid is produced in high yields and purity by heating urea in a dialkylamide solvent, such as DMAC. The use of DMAC has the additional advantage that this compound is a good solvent for urea but not for cyanuric acid and thus facilitates the recovery of the cyanuric acid (13).

Dimethylacetamide, as well as other dialkylamides, increases the yields of nitriles and decreases the by-products formed in the reactions of alkyl halides and metal cyanides (14).

Sodium acetylide fails to react with alkyl halides in conventional solvents, such as dioxane, xylene, or dibutyl ether. However, it does react in solvents such as DMAC to yield alkylacetylenes. The effect of the solvent here was shown to be catalytic (15).

Organic isocyanates (see Isocyanates, organic) may be prepared in higher yields than were previously known by reacting alkali or alkaline earth cyanates with organic halides in dialkylamide solvents, such as DMAC. The advantages gained by using these solvents in the preparation of benzyl isocyanate have been cited specifically (16).

DMAC proved to be a very suitable solvent for interesterification. In the preparation of fatty acid esters of sucrose, it gives rapid reaction rates with minimum decomposition (17).

In the preparation of α,α -disubstituted α -phthalimidoacetic acids (from phthalic anhydride and the appropriate substituted aminoacetic acid), the use of solvents of the dialkylamides, such as DMAC, increased both yields and reaction rates (18).

Dimethylacetamide serves as a catalyst in the formation of organic sulfonyl chlorides from the corresponding sulfonic acids by the use of thionyl halide or phosphorus oxyhalide. Rapid reaction rates at room temperatures are possible due to the catalytic effect of the dialkylamides (19).

Formation of Complexes. Dimethylacetamide, like other dialkylamides, is a highly polar solvent and thus forms numerous crystalline solvates and complexes. Because of the complex that it forms with hydrogen cyanide, the use of DMAC as a reaction medium for hydrocyanations has been pointed out as an advantage. The complexes have vapor pressures lower than predicted, and thus lower reaction pressures are possible (20).

Electrolytic Solvent. The use of dimethylacetamide as a nonaqueous electrolytic solvent is promising because salts are moderately soluble in DMAC and appear to be completely dissociated in dilute solutions (21).

Paint Remover. Dimethylacetamide is of interest as a solvent in paint stripping because of its very rapid removal action when used alone or in combination with methylene chloride. It has been found to be superior to other common solvents such as nitromethane, methyl ethyl ketone, or methanol (22).

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Acetanilide

Acetanilide (acetanilid, USP XIII, *N*-phenylacetamide, *N*-acetylaniline, Antifebrin), $\text{C}_6\text{H}_5\text{NHCOCH}_3$, molecular weight 135.16, forms colorless, lustrous crystal scales but can also be obtained as a white powder. It is a stable compound and can be boiled without decomposition. The little-known unstable, monoclinic (?) form goes over into the stable, rhombic form. Acetanilide was first prepared by Gerhardt in 1852 by the reaction of aniline and acetyl chloride. The first recorded medicinal use was by Cahn and Hepp in 1886. It is a useful starting material in organic synthesis because of the protective action of its acetyl group on the amino group, which is readily freed by hydrolysis. A modern instance is the synthesis of certain sulfa drugs. Antifebrin, though still used in pharmaceutical compounding, has been largely superseded by acetophenetidin (Phenacetin), particularly as an antipyretic (as which it was formerly used).

Physical Properties. Mp, 114.2°C (ICT); bp, 303.8°C (cor) (ICT); d_4^{20} , 1.21; d_4^{120} , 1.0261; heat capacity (mean: 0–99.6°C), 0.3391 cal/g; heat of vaporization at 154°C, 136 cal/g; heat of combustion, 1010.4 kcal/gram-mole; ionization constant (K_i) at 40°C, 4.1×10^{-14} ; cryoscopic constant ($K_F = \Delta T/N$), 6.932; dielectric constant

Table 1. Boiling Point Elevation in Aqueous Solution (1)

<i>N</i>	Δt_B
0.3	19.0
0.4	17.9
0.45	17.3

(ϵ), 19.5; dipole moment, 4.01; viscosity at 120°C, 0.0222 g/cm-sec; surface tension at 118°C, 32.9 dynes/cm.

Boiling point elevation in aqueous solution (Δt_B) at normal atmospheric pressure is shown in Table 1 (N = gram-moles per kg of water). Acetanilide crystallizes from water in the form of rhombic leaflets, or scales having two axes of symmetry.

The solubilities of acetanilide in various solvents are shown in Tables 2, 4, and 5. The liquid layers that separate above 83.2°C in aqueous solutions have the compositions shown in Table 3.

Table 2. Solubility of Acetanilide in Water (2)

Temper- ature, °C	Acetanilide, g/100 g satd soln	Solid phase	Temper- ature, °C	Acetanilide, g/100 g satd soln	Solid phase
−0.03 (eutectic)	0.5	ice + acetanilide	80.0	4.5	acetanilide
15.0	0.5	acetanilide	83.2	5.2 (quad pt)	acetanilide + 2 liquid layers
20.0	0.52	acetanilide	83.2	87.0	acetanilide + liquid layers
30.0	0.63	acetanilide	85.0	91.0	acetanilide
40.0	0.86	acetanilide	90.0	94.5	acetanilide
50.0	1.25	acetanilide	95.0	96.5	acetanilide
60.0	2.0	acetanilide	100.0	97.0	acetanilide
70.0	3.0	acetanilide	114.0	100.0 (mp)	acetanilide

Courtesy American Chemical Society.

Table 3. Compositions of Liquid Layers of Aqueous Solutions (2)

Temperature, °C	Acetanilide, g/100 g		Temperature, °C	Acetanilide, g/100 g	
	Water-rich layer	Acetanilide- rich layer		Water-rich layer	Acetanilide- rich layer
83.2	5.2	87.0	135.0	22.0	69.0
90.0	5.8	82.5	140.0	28.0	63.0
100.0	6.5	80.5	142.0	30.0	60.0
120.0	13.0	79.0	144.0	45.0	45.0
130.0	18.0	73.0	(crit temp)		

Courtesy American Chemical Society.

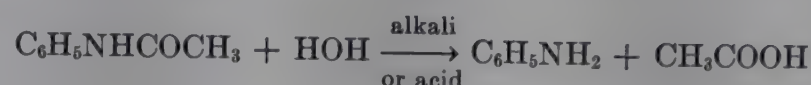
Table 4. Solubility of Acetanilide in Organic Solvents (3)

Solvent	Temper- ature, °C	Acetanilide, g/100 g satd soln	Solvent	Temper- ature, °C	Acetanilide, g/100 g satd soln
ether	25	7.7	amyl acetate	30–31	10.46
chloroform	25	16.6	aniline	30–31	19.38
acetone	30–31	31.15	amyl alcohol	25	14.00
benzene	30–31	2.46	xylene	32.5	1.65
benzaldehyde	30–31	18.83	ethyl alcohol	20.0	36.9

Table 5. Solubility of Acetanilide in Aqueous Acetic Acid Solutions

Acetic acid, % (wt/wt)	Acetanilide, g/100 g acetic acid soln			
	20°C	25°C	30°C	35°C
21.2	2.23	2.70	3.28	4.05
34.4	9.82	12.2	15.3	19.2
43.4	31.5	38.2	46.6	56.9
45.9	40.4	47.6	56.7	67.9
47.7	45.4	52.5	61.2	71.6
49.7	46.2	52.9	60.9	70.7

Chemical Properties. Acetanilide is mildly basic. Though stable under ordinary conditions, it hydrolyzes readily when heated with aqueous alkali or with aqueous mineral acid solutions.



This property is carried over to its derivatives and is useful in the synthesis of nuclear-substituted phenylamines (see under Uses). When heated with zinc chloride at 250°C, acetanilide condenses to form the unimportant yellow dye, Flavaniline (CI 804). The acetamido group ($\text{CH}_3\text{CONH}-$) of acetanilide is strongly para-directing, or, if the para position is filled, ortho-directing. The *N*-hydrogen atom is readily replaceable under suitable conditions to form *N*-substituted compounds.

Pyrolysis products of acetanilide are *N,N'*-diphenylurea, aniline, benzene, and hydrocyanic acid. Passage of dry hydrogen chloride into molten acetanilide produces *N,N'*-diphenylacetamidine, $\text{CH}_3\text{C}(=\text{NC}_6\text{H}_5)\text{NHC}_6\text{H}_5$. Addition of sodium to a hot solution of acetanilide in xylene produces the *N*-sodium derivative. Chlorine replaces oxygen, giving $\text{C}_6\text{H}_5\text{NHCCl}_2\text{CH}_3$, which loses HCl to give $\text{C}_6\text{H}_5\text{N}=\text{CClCH}_3$. When heated with phosphorus pentasulfide, acetanilide yields thioacetanilide, $\text{C}_6\text{H}_5\text{NHCSCCH}_3$, from which thioimido compounds, amidines, etc, can be prepared. When treated with hydrochloric acid, acetanilide in acetic acid solution gives the two salts $2 \text{C}_6\text{H}_5\text{NHCOCH}_3 \cdot \text{HCl}$ and $\text{C}_6\text{H}_5\text{NHCOCH}_3 \cdot \text{HCl}$. When treated with bromine, acetanilide in aqueous acetic acid solution yields *p*-bromoacetanilide ($p\text{-BrC}_6\text{H}_4\text{NHCOCH}_3$); in aqueous solution containing potassium bicarbonate, it yields *N*-bromoacetanilide ($\text{C}_6\text{H}_5\text{NBrCOCH}_3$). The reactions with chlorine are analogous. The corresponding iodo derivative is obtained by the action of iodine monochloride in acetic acid or molecular iodine and mercuric acetate on acetanilide. Nitration of acetanilide in sulfuric acid solution yields predominantly *p*-nitroacetanilide, $p\text{-NO}_2\text{C}_6\text{H}_4\text{NHCOCH}_3$ (4). When acetanilide is treated with excess chlorosulfonic acid at elevated temperatures, the important reaction product is *N*-acetylsulfanilyl chloride, $p\text{-CH}_3\text{-CONHC}_6\text{H}_4\text{SO}_2\text{Cl}$. Heating with aluminum chloride at 188–200°C for 10 hours, produces a 15% yield of *p*-aminoacetophenone (5). Trichloroacetanilide ($\text{C}_6\text{H}_5\text{NHCOCCL}_3$) is obtained in 40–80% yield by heating acetanilide with trichloroacetic acid at 120–130°C for 8 to 14 hours (6). Reduction of acetanilide with lithium aluminum hydride in ethyl ether or sodium aluminum hydride in tetrahydrofuran affords a 93 or 63% yield, of *N*-ethylaniline, respectively. Acetanilide undergoes alcoholysis with methanol–borontrifluoride or isoamyl alcohol–aluminum triamyloxyde to produce aniline.

Manufacture and Preparation. Methods 1 and 2 are the most practical procedures in use today. Methods 3 to 6 represent other possible syntheses.

1. *From acetic anhydride and aniline.* A benzene solution of one part of aniline and 1.4 parts of acetic anhydride is refluxed in a jacketed, enameled still until no free aniline remains.



The reaction mixture is filtered, and the crystals separating on cooling are recrystallized from hot water. Acetyl chloride may be used in place of acetic anhydride.

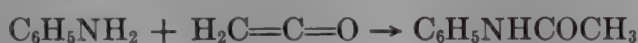
2. *From acetic acid and aniline.* This method, though one of the earliest, is still in use because of its economy. Aniline and about 100% molar excess of acetic acid (degree of excess depending on strength) is refluxed from 6 to 14 hours in a suitable still. Glacial acetic acid is preferred industrially.



If the acetic acid is quite dilute or if crude pyroligneous acid is used, the reaction is carried out under pressure at 150–160°C. The product is dropped into water (usually hot) and allowed to crystallize.

In another modification (7), the aniline is heated to its boiling point and heating is continued while acetic acid is added slowly during the course of the reaction. The reaction is carried out under nonoxidizing conditions, at about 110°C, and in 6 hours.

3. *From ketene and aniline.* Ketene (gas) when passed into aniline under suitable conditions produces acetanilide (8,9).

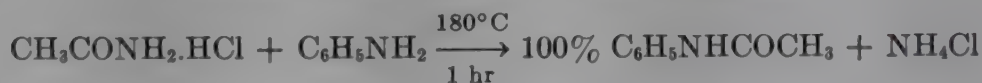


At present, this process appears to be industrially uneconomical.

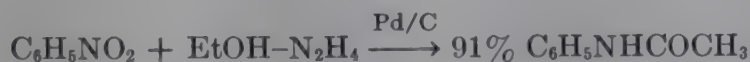
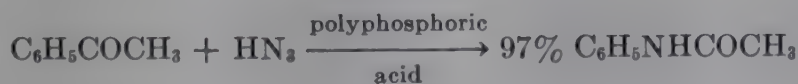
4. *From thioacetic acid and aniline.* Thioacetic acid reacts with aniline, in the cold, to give acetanilide with the liberation of hydrogen sulfide.



5. *From acetonitrile or acetamide,*



6. *Other reported methods* are given in the following equations (see refs. 10, 11, and 12, respectively).



GRADES AND SPECIFICATIONS

USP-grade acetanilide comes in the following containers: 1-oz, 4-oz, 1-lb, 5-lb, 25-lb, and 50-lb cartons; 100-lb kegs; 100-lb, 150-lb, 170-lb, and 200-lb barrels. Technical-grade acetanilide comes in 200-lb barrels and 200-lb paper bags (moistureproof). (All weights are net.) Railroad classification is as follows: acetanilide, NOIBN. Acetanilide has no unusual hazard; inhalation of its dust should be avoided.

Table 6. Grades of Acetanilide

Property	Technical (13)	USP (14)
form	flakes or powder	crystals or powder
color	white to cream	white
ash	0.2% max	0.05% max
melting point	—	114.0°C min
setting point	112.0°C min	—
solubility		
in 95% ethyl alcohol	—	complete
in glacial acetic acid	complete	—
fineness		
14-mesh	—	none
80-mesh	—	3.0% max
free aniline	0.2% max	none
free acetic acid	0.75% max	none

TESTS

For details of tests on USP material, consult references 4 and 6. The free-aniline content is determined most conveniently by a colorimetric method (13). Free acetic acid content is obtained by titrating in alcoholic solution with standard alkali. Identification tests for acetanilide (USP, USD) are as follows: (1) Boil with dilute alkali—a characteristic odor of aniline results. (2) Treat saturated solution with bromine water—a white precipitate of *p*-bromoacetanilide is obtained. (3) Warm with potassium hydroxide and chloroform—a disagreeable odor of phenyl isocyanide (poison) evolves.

Uses. Acetanilide is used as an antipyretic and analgesic (qv). Its use as an antiseptic is diminishing. It is also employed in the manufacture of the dye intermediates *p*-nitroacetanilide, *p*-nitroaniline, and *p*-phenylenediamine, and of the derivatives mentioned below. During World War II considerable quantities went into the manufacture of acetylsulfanilyl chloride. Acetanilide is also used in the preparation of thioacetanilide.

Other possible applications of acetanilide include its use as a stabilizer for both hydrogen peroxide and for cellulose; as an additive in cellulose ester type lacquers; and as a rubber accelerator.

Important Derivatives. *p*-Bromoacetanilide (Bromoanilid, Antisepsin, Asepsin), $p\text{-BrC}_6\text{H}_4\text{NHCOCH}_3$, white crystals, mp 168°C, is insoluble in water, moderately soluble in alcohol, and easily soluble in benzene and chloroform. It is prepared by the action of bromine on acetanilide in acetic acid solution. Although it is used as an analgesic and antipyretic, large doses may cause cyanosis.

N-Acetylsulfanilyl chloride (*p*-acetamidobenzenesulfonyl chloride or *p*-acetylaminobenzenesulfonyl chloride, abbreviated to ASC in sulfa-drug terminology), $p\text{-CH}_3\text{CONHC}_6\text{H}_4\text{SO}_2\text{Cl}$. The industrial product is a gray to white, granular to crystalline material, mp about 149°C. It is unstable in the presence of moisture and impurities, insoluble in water, and soluble in acetone and hot ethylene dichloride. *N*-Acetylsulfanilyl chloride was first prepared by Gelmo in 1906. It is produced industrially by allowing acetanilide to react with excess chlorosulfonic acid at elevated temperatures (15). Its chief use is in the manufacture of sulfa drugs (qv). ASC condenses readily with primary amines; for example, with 2-aminothiazole it gives acetylsulfathiazole, which on hydrolysis yields sulfathiazole.

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ACETIC ANHYDRIDE, $(\text{CH}_3\text{CO})_2\text{O}$. See Ethanoic acid.

ACETINS (acetates of glycerol). See Glycerol.

ACETOACETIC ACID AND ESTER

Acetoacetic Acid

Acetoacetic acid (acetylacetic acid, β -ketobutyric acid, acetone monocarboxylic acid), $\text{CH}_3\text{COCH}_2\text{COOH}$ (abbreviated as AcCH_2COOH), formula weight 102.0, is not a commercial chemical, and is less well known than its esters. Like other β -ketoacids it is very unstable either as the free acid or as its salts. The esters and amides of acetoacetic acid, however, are stable, can be purified without decomposition, and serve as extremely valuable intermediates in organic syntheses. The free acid is obtained by hydrolyses of its esters with cold aqueous potassium hydroxide (the rate of hydrolysis is independent of the concentration); the resulting solution is acidified, extracted with ethyl ether, and the ethereal solution is dried in a desiccator over sulfuric acid. Acetoacetic acid is a strongly acid syrupy substance which is miscible with water in all proportions. When dissolved in warm water or when heated, it spontaneously decomposes into acetone and carbon dioxide. Because of its high instability, purification is difficult and rarely attempted.

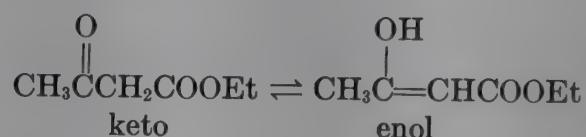
When acetoacetic acid is treated with nitrous acid, oximidoacetone (isonitrosoacetone), $\text{CH}_3\text{COCH}=\text{NOH}$, and carbon dioxide are immediately formed. Because of its high enolic content (see below), a red-violet coloration is observed with ferric chloride.

The aldol condensation of aldehydes with acetoacetic acid has been used in biosyntheses. It is an intermediate product in the metabolism of fat by the oxidation of butyric acid. Because diabetics are incapable of catabolizing acetoacetic acid to acetic acid, acetoacetic acid and acetone are found in their urine.

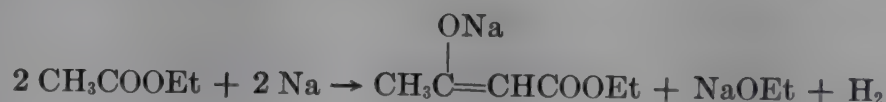
Acetoacetic Ester

Acetoacetic ester (ethyl acetoacetate, ethyl β -ketobutyrate, ethyl acetylacetate), $\text{CH}_3\text{COCH}_2\text{COOC}_2\text{H}_5$ (abbreviated as $\text{AcCH}_2\text{COOEt}$), formula weight 130.14, is commercially available as a colorless, stable oil which has a rather refreshing odor.

In 1863, Geuther reported a compound, $\text{C}_6\text{H}_{10}\text{O}_3$, obtained upon acidification of the product from the reaction of ethyl acetate with sodium. Because this substance demonstrated properties characteristic both of an acid and an ester, he called it "ethyl diacetic acid." Simultaneously, but quite independently, Frankland and Duppa isolated the same product from the reaction of sodium and alkyl iodides on ethyl acetate and assigned to it the structure of a ketobutyric acid. In 1877, Wislicenus clarified the structure and we now write acetoacetic ester as a tautomeric mixture of keto and enol forms existing in dynamic equilibrium.



The reaction of sodium with ethyl acetate proceeds according to the equation



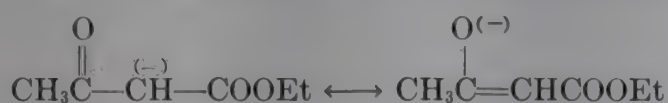
giving the sodium derivative of the enol form, *ethyl sodioacetoacetate*.

It has been shown that freshly prepared ethyl acetoacetate consists of 7.7% enol and 92.3% keto forms and that this ratio is affected by solvents and temperature. This ratio has been corroborated by refractive index measurements and by quantitative ultraviolet analyses. Each form can be isolated, in a rather high state of purity, but on standing they equilibrate. The keto form is isolated by cooling an alcoholic or petroleum ether solution of ethyl acetoacetate to -78°C . The enol form has also been isolated, at -78°C , by treating a suspension of the sodium salt with hydrogen chloride followed by removal of the sodium chloride and solvent. Unlike the keto form, freshly prepared enol gives a red color with ferric chloride and reacts with molecular bromine. A more convenient method for isolating the enol form involves treating ethyl sodioacetoacetate with acetyl chloride in ethyl ether followed by hydrolysis of the resultant acetate with dilute oxalic acid.

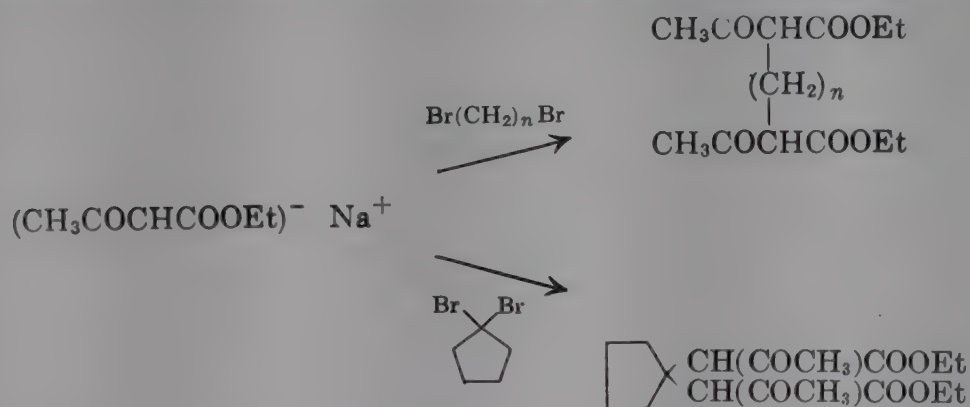
The equilibrium reaction, keto \rightleftharpoons enol, is catalyzed by minute traces of acid or alkali. Thus, by using an all-quartz apparatus (aseptically clean), it is possible to obtain pure enol and keto forms by a careful, direct fractionation. Because the enol is more volatile, the proportion of enol content is increased from 7.3% to 20–30% upon direct distillation in glass equipment.

Physical Properties. Mp, -39°C (keto) and -44°C (enol); bp, 180°C (755 mm), 71°C (12.5 mm), 41°C (2 mm); d_4^{20} , 1.025; n_D^{20} , 1.41976; n_D^{10} , 1.4225; C_p at 24.4°C , 59.80 cal/mole; heat of dissociation (in water at 20°C), -6.37 kcal/mole; dissociation constant ($25.0 \pm 0.1^{\circ}\text{C}$), $2.09 \pm 0.02 \times 10^{-11}$; vapor pressure at 20°C , 0.8 mm Hg; absolute viscosity at 20°C , 1.6 cps; flash point (open cup), 185°F ; solubility in water at 20°C , 11.6% by weight. Acetoacetic ester is combustible but not flammable.

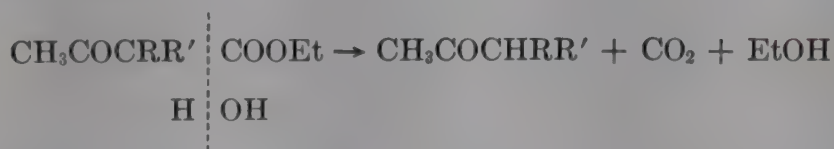
Chemical Properties. In acetoacetic ester there are three reactive groups: a carbonyl, a carbethoxy ($-\text{COOC}_2\text{H}_5$) and an active methylene group. Moreover, because of the resonance hybrid representing its anion, acetoacetic ester under alkaline



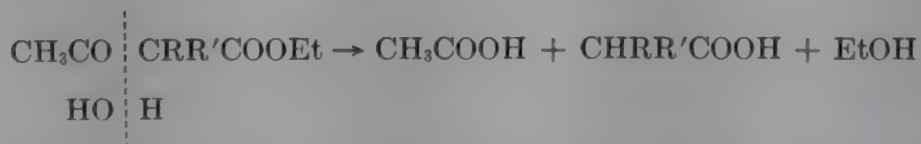
conditions can react to form an O- or C-substituted derivative. Thus, the sodium salt reacts with alkyl halides (RX) to produce homologous β -keto esters, $\text{CH}_3\text{COCHR}-\text{COOEt}$. Because the product still contains an enolizable hydrogen atom, its anion can react further with another mole of the alkyl halide or a different alkyl halide ($\text{R}'\text{X}$) to produce a dialkylated β -keto ester, $\text{CH}_3\text{COCRR}'\text{COOEt}$. Acetoacetic ester may also be alkylated with dihalides to produce some rather interesting organic molecules.



These homologous acetoacetic esters can be hydrolyzed in two different ways to give a ketone or an acid. Dilute mineral acids or alkalies react to produce a ketone, carbon dioxide, and ethyl alcohol.



Strong alkali, especially alcoholic alkali, produces acetic acid, a carboxylic acid, and ethyl alcohol.



Thus, substituted ketones and carboxylic acids can be easily prepared. The yields of acids are generally good, but based on the economics involved, malonic ester (see Malonic acid) is usually preferred for the syntheses of long-chain acids; fewer side reactions are also encountered.

Sodium salts of monosubstituted ethyl acetoacetates ($\text{CH}_3\text{COCRCOOEt}-\text{Na}^+$) react with acid chlorides ($\text{R}'\text{COCl}$) or chloroformic esters to give the expected

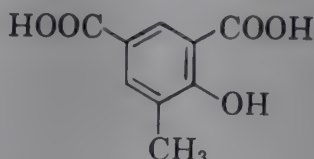
C-acylated product, $\text{CH}_3\text{COCR}(\text{COR}')\text{COOEt}$; in the presence of pyridine the free ester reacts with acid chlorides to produce O-acylation, $\text{CH}_3\text{C}(\text{OCOR}')=\text{CRCOOEt}$.

Iodine converts sodioacetoacetic ester to diacetosuccinic ester.

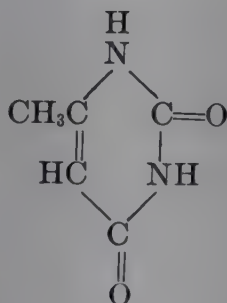


In the presence of sodium ethoxide, ethyl acetoacetate reacts with ethylene oxide to produce α -acetobutyrolactone which has found considerable use in drug manufacture (see under Uses and applications).

Chloroform, chloral, or ethyl trichloroacetate reacts with ethyl sodioacetoacetate to form 4-hydroxyuvitic acid (4-hydroxy-5-methylisophthalic acid).

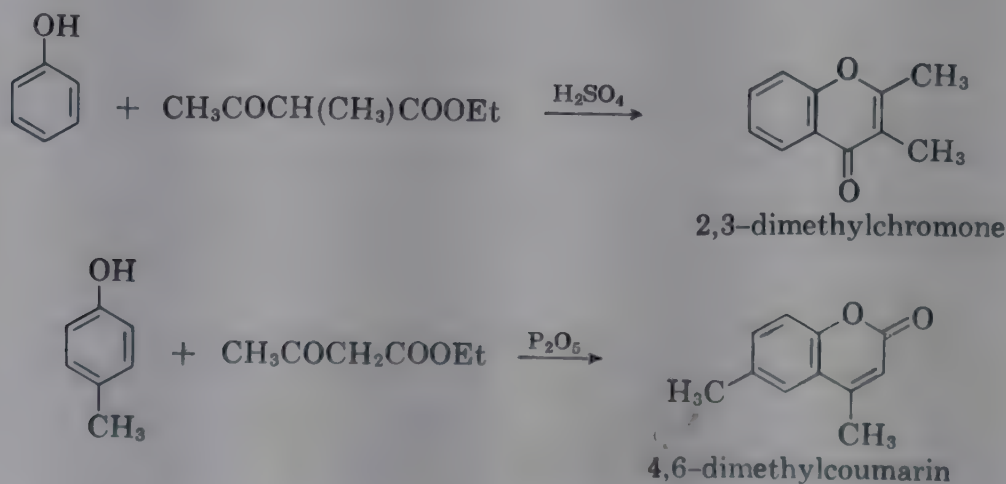


Ethyl acetoacetate undergoes the normal carbonyl reactions expected of a ketone, such as cyanohydrin formation and sodium bisulfite addition. It is readily hydrogenated to form ethyl β -hydroxybutyrate, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{COOEt}$; reacts with diazomethane to produce β -methoxycrotonic ester, $\text{CH}_3\text{C}(\text{OCH}_3)=\text{CHCOOEt}$; reacts with urea to form 6-methyluracil,



which is the parent substance in the synthesis of uric acid (qv) and reacts with amidines to produce pyrimidine compounds.

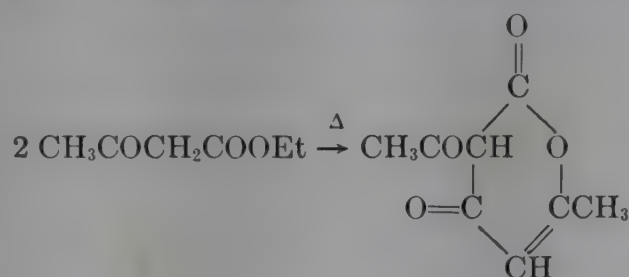
Ethyl acetoacetates condense with phenols and quinones to give either coumarins or chromones, depending on the nature of the phenol or quinone and on the condensing agent. Thus,



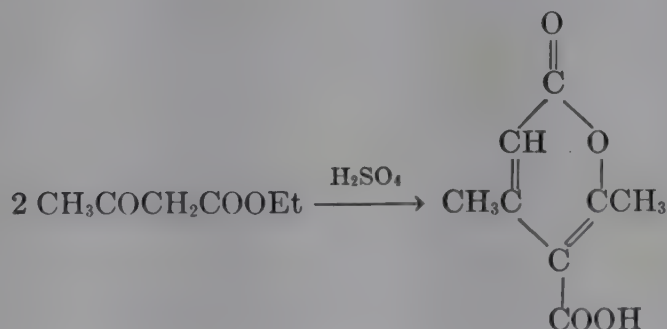
Because of the enol content, acetoacetic ester undergoes facile substitution on the α -carbon by halogen. With chlorine the α -chloro and/or the α,α -dichloro compounds

are prepared; with bromine, the α -bromo compound is unstable and rearranges to the γ -derivative ($\text{BrCH}_2\text{COCH}_2\text{COOEt}$) whereas the α,α -dibromo compound is quite stable. (Actually, the location of the bromine atom in the monobromo derivative is disputable.) Phosphorus pentachloride reacts with the ester in such a manner as to replace the ketonic oxygen; the product is ethyl 3,3-dichlorobutyrate ($\text{CH}_3\text{CCl}_2\text{CH}_2\text{COOEt}$). Orthoformic ester reacts analogously to produce the 3,3-diethoxy derivative; this ketal readily loses alcohol to give β -ethoxycrotonic ester. Nitrous acid converts acetoacetic ester to the oximido derivative ($\text{CH}_3\text{COC}(=\text{NOH})\text{COOEt}$) which decomposes readily into oximidoacetone. This oximido compound can be partially reduced to $\text{CH}_3\text{COCH}(\text{NH}_2)\text{COOEt}$, used in the Knorr synthesis of pyrroles (qv), or fully reduced and hydrolyzed to the important amino acid threonine ($\text{CH}_3\text{CHOHCHNH}_2\text{COOH}$). (See Amino acids.)

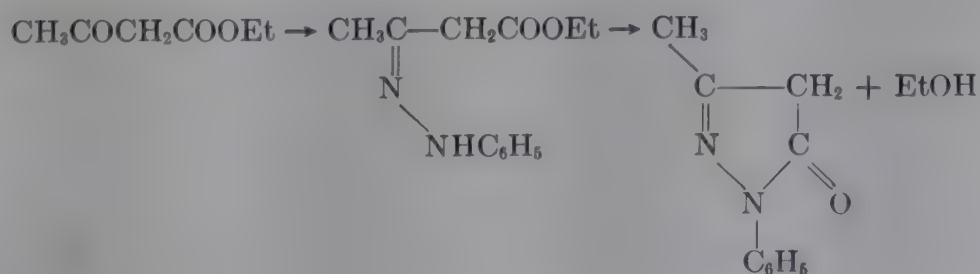
When ethyl acetoacetate is heated alone, it loses ethyl alcohol and forms *dehydroacetic acid* (3-acetyl-6-methyl-2*H*-pyran-2,4(3*H*)-dione), the δ -lactone of an



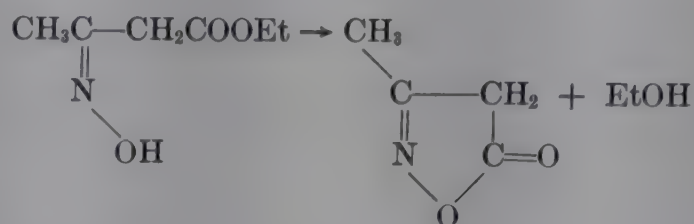
unsaturated δ -hydroxydiketone carboxylic acid. The prolonged action of concentrated sulfuric acid causes it to pass into a condensation product, *isodehydroacetic acid* (4,6-dimethylcoumalic acid), the δ -lactone of an unsaturated δ -hydroxydicarboxylic acid.



Ammonia, aniline, hydrazine, and phenylhydrazine react with acetoacetic ester to give the imine, anilide, hydrazone, and phenylhydrazone, respectively. These are tautomeric with the β -amino, β -anilino, β -hydrazino, and β -phenylhydrazino crotonic esters. All of these compounds readily lose alcohol and produce cyclic compounds. Thus, the phenylhydrazones are key intermediates in the formation of pyrazolones.



The anilide, $\text{CH}_3\text{COCH}_2\text{CONHC}_6\text{H}_5$, gives 2-hydroxy-4-methylquinoline (4-methyl-carbostyrl) upon treatment with warm sulfuric acid. The oxime formed by treating acetoacetic ester with hydroxylamine loses alcohol and cyclizes to methylisoxazolone (3-methyl-2-isoxazolin-5-one).



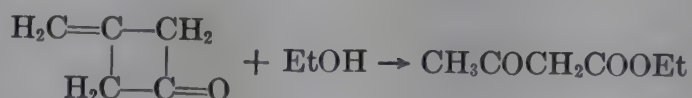
Hence, these reactions provide a synthetic route to a wide variety of heterocyclic ring systems.

Aldehydes, such as acetaldehyde, react with ethyl acetoacetate (Knoevenagel reaction) to produce alkylidene mono- and alkylidene bisacetoacetic esters. The former, $\text{RCH}=\text{C}(\text{COCH}_3)\text{COOEt}$, are readily hydrogenated to α -alkyl derivatives, $\text{CH}_3\text{COCHR}'\text{COOEt}$ ($\text{R}' = -\text{CH}_2\text{R}$), and therefore provide an alternative route to the sodioacetoacetic ester-alkyl halide route. The alkylidene bisacetoacetic esters, $\text{RCH}(\text{CH}(\text{COCH}_3)\text{COOEt})_2$, undergo intramolecular condensation, accompanied by loss of water, to produce a cyclohexanone derivative, or react with ammonia (Hantzsch pyridine synthesis) to give a hydropyridine derivative (see Pyridine).

Acetoacetic ester undergoes direct cyanoethylation with acrylonitrile in the presence of a strong quaternary hydroxide (Triton B) to produce ethyl 2,2-bis(2-cyanoethyl)-3-ketobutanoate, $(\text{CNCH}_2\text{CH}_2)_2\text{C}(\text{COCH}_3)\text{COOEt}$. Acetoacetic ester also reacts with certain divalent metals, such as copper, to give a stable crystalline covalent chelate.

Preparation; Manufacture; Commercial Availability. Ethyl acetoacetate is most conveniently prepared by allowing high-purity ethyl acetate to react with metallic sodium. The sodium derivative is neutralized with sulfuric acid and the crude ester is separated and purified by vacuum distillation. The yield is better than 90%.

An alternative commercial preparation involves the reaction of diketene with ethanol; the yield is reportedly 95%.

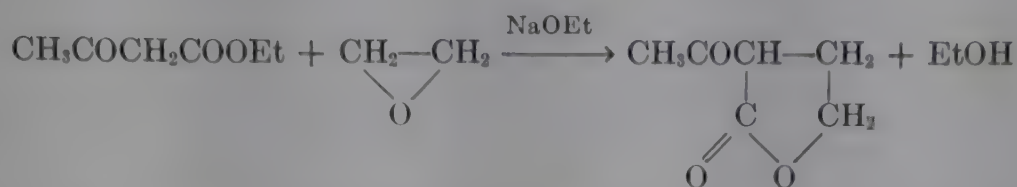


Ethyl acetoacetate is shipped in 1-gal glass jugs (8 pounds), 5-gal glass-stoppered carboys (40 pounds), and 55-gal stainless steel drums (450 pounds). As of May 1962, ethyl acetoacetate was priced at \$0.58–0.59 per pound in drum quantities.

Uses and Applications. Acetoacetic ester is used academically as well as industrially in the synthesis of many heterocyclic ring systems—coumarins, chromones, pyridines, isoxazolones, pyrazolones, pyrimidines, pyrroles, and lactones, and in the syntheses of cyclohexanone derivatives. Because of the relative ease with which α -alkylated derivatives are cleaved, it has served as an invaluable intermediate in the syntheses of many ketones and carboxylic acids.

The anilides formed by condensation of acetoacetic ester with ring-substituted anilines are used in the preparation of Hansa colors. These yellow pigments are used in the manufacture of paint, lacquer, and ink. Pyrazolones prepared from the phenylhydrazones are used in the formation of photographic dyes as well as vat

dyes. Atabrine, methionine, and thiamine are manufactured from α -acetobutyrolactone.



Novaldiamine, an intermediate in the manufacture of antimalarial drugs, may be prepared from acetoacetic ester and diethylethanolamine (2-diethylaminoethanol). Antipyrine and aminopyrine, used as antipyretics and analgesics, are derived from 3-methyl-1-phenyl-2-pyrazolin-5-one (see under Chemical properties).

“Acetoacetic Acid Esters” treated in *ECT* 1st ed. under “Esters, Organic,” Vol. 5, pp. 845–849, by Dora Stern, Elsevier’s Encyclopædia of Organic Chemistry.

ARNOLD P. LURIE
Eastman Kodak Company

ACETONE

Acetone (dimethyl ketone, 2-propanone (IUPAC)), CH_3COCH_3 , formula weight 58.079, is the simplest and most important of the ketones. It is a colorless, mobile, flammable liquid with a mildly pungent and somewhat aromatic odor. It is miscible in all proportions with water and with organic solvents such as ether, methanol, ethyl alcohol, and esters. Acetone is used as a solvent for cellulose acetate, nitrocellulose, and acetylene and as a raw material for the chemical synthesis of such products as ketene, acetic anhydride, methyl methacrylate, bisphenol A, diacetone alcohol, mesityl oxide, methyl isobutyl ketone, hexylene glycol, and isophorone.

Acetone was first observed in about 1595 by Libavius, who obtained it by dry distillation of sugar of lead (lead acetate). In 1805, Trommsdorff stated that on distillation of “acetate of potash or soda” he obtained a liquid intermediate between alcohol and ether. The correct composition of acetone was first determined in 1832 by Liebig and Dumas. Some years later, Williamson ascertained the constitution of the ketones and considered acetone to be methylacetyl. The synthesis of acetone by the action of dimethylzinc on acetyl chloride confirmed this view.

Properties

Physical and Thermodynamic Properties. Melting point, -94.6°C ; boiling point, 56.1°C at 760 mm; d_4^{20} , 0.7898; n_D^{20} , 1.3588; vapor pressure, 180.3 mm Hg at 20°C ; specific heat of liquid, 0.5176 cal per gram at 20°C ; heat of vaporization, 6952 cal per mole at 56.1°C and 760 mm; specific heat of vapor, C_p , 22 cal/(degree) (mole) at 102°C ; viscosity, 0.316 cps at 25°C ; electrical conductivity, 5.5×10^{-8} ohm $^{-1}$ cm $^{-1}$ at 25°C ; heat of combustion of liquid, 427 kcal per mole (7.37 kcal per gram); heat of formation at 25°C , gas -51.72 kcal per mole, liquid -59.25 kcal per mole; entropy of liquid at 298.15°K, 47.82 (1).

Chemical Properties. Acetone shows the typical reactions of ketones (qv). It forms crystalline compounds with alkali bisulfites; for example, with sodium bisulfite, the compound $(\text{CH}_3)_2\text{C}(\text{OH})\text{SO}_3\text{Na}$ is obtained. Reducing agents convert acetone to

isopropyl alcohol, $\text{CH}_3\text{CHOHCH}_3$, and pinacol $(\text{CH}_3)_2\text{COHCOH}(\text{CH}_3)_2$. Acetone is not easily oxidized. It is unaffected by nitric acid (d 1.37) unless heated above room temperature, and is stable to neutral permanganate. The more powerful oxidizing agents, such as alkaline permanganate and chromic acid, break it down to acetic and formic acids; the formic acid is oxidized further to carbon dioxide and water. Acetone does not reduce ammoniacal silver or Fehling's solution. The flash point of acetone is -18°C by the closed-cup method. The explosive limits of acetone-air mixtures appear to lie between 2.15 and 13.0 percent by volume of acetone in air at room temperature.

Occurrence and Formation

Acetone occurs in small quantities in human blood and normal urine and in considerable amounts in the urine of diabetics as a decomposition product of acetoacetic acid, $\text{CH}_3\text{COCH}_2\text{COOH}$. Acetone is contained in small amounts in pyroligneous acid, which results from the dry distillation of wood (see Wood). It is also formed by thermal decomposition of coal, peat, acetic acid salts, formates, and citric acid, and by the dry distillation of sugars or gums with lime. Acetone is formed when acetic acid is passed over catalysts such as aluminum oxide, thorium oxide, zinc oxide, and titanium oxide at $300\text{--}400^\circ\text{C}$. The chemical oxidation of isopropyl alcohol with hydrogen peroxide, with nitric oxide in alkaline solutions, or with alkaline permanganate, gives acetone. Isopropyl alcohol is also converted to acetone by vapor-phase dehydrogenation or oxidation at elevated temperatures in the presence of catalysts. Such miscellaneous reactions as the addition of water to a solution of allylene in concentrated sulfuric acid, the hydrolysis of propylene chloride, and the heating of formaldehyde or acetaldehyde with dimethylamine also result in the formation of acetone (2).

Manufacture

Until World War I, acetone was manufactured in the United States by the dry distillation of calcium acetate, which, in turn, was obtained by neutralizing pyroligneous acid with lime and evaporating to dryness (3). World War I caused a sharp increase in the requirements for acetone which could not be met by the wood distilling industry. To supplement the limited production from wood distillation, some calcium acetate was made from acetic acid produced by fermentation of alcohol or from acetylene (4). However, these sources could not compete with the fermentation process developed by Chaim Weizmann (5) for the conversion of carbohydrates to acetone and butyl alcohol by means of a special bacillus. This process supplied most of the acetone required during World War I and the early 1920s.

Production of acetone by dehydrogenation of isopropyl alcohol began in the middle 1920s and soon displaced fermentation as the predominant process. At present, about three-fourths of United States acetone is made by this process. The remainder is made as a coproduct in the following processes:

1. The cumene hydroperoxide process for phenol and acetone (6). Benzene is alkylated to cumene (isopropylbenzene), which is oxidized to cumene hydroperoxide. The latter is easily cleaved to phenol (qv) and acetone.

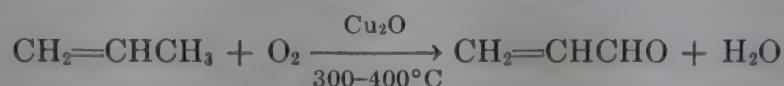


2. Direct oxidation of propane-butane mixtures to a number of oxygenated products including acetone (7). (See Hydrocarbon oxidation.)

3. Fermentation of carbohydrates by special bacilli to acetone and butyl alcohol.

4. Shell Chemical Company's new glycerin process in which acetone is obtained as a by-product (8). (See Glycerol.) An outline of this process is shown schematically in Figure 1. The various steps can be briefly described as follows:

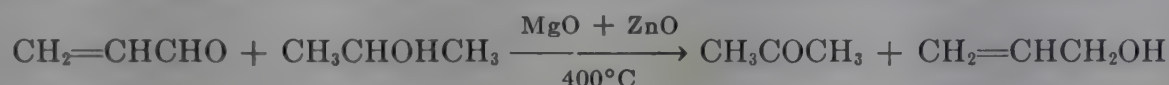
Propylene is oxidized to acrolein in a vapor-phase catalytic reaction.



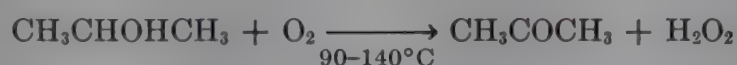
Propylene is absorbed, under a pressure of several atmospheres, in sulfuric acid, forming isopropyl sulfate, which is hydrolyzed to isopropyl alcohol.



The acrolein is reacted with isopropyl alcohol to give acetone and allyl alcohol.



Pure oxygen is bubbled through liquid isopropyl alcohol, forming acetone and hydrogen peroxide.



The allyl alcohol is converted to glycerol by reaction with the hydrogen peroxide.

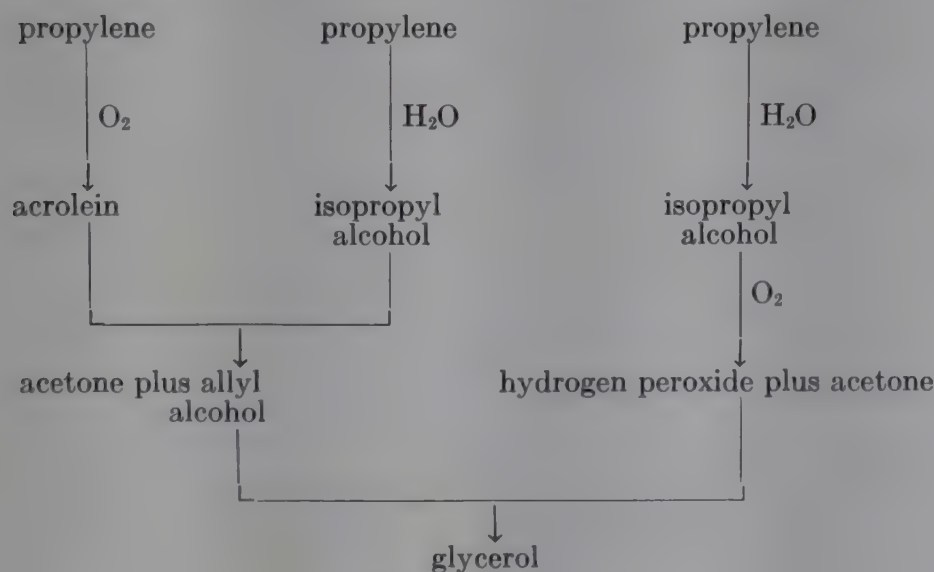
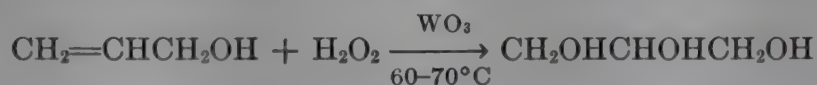
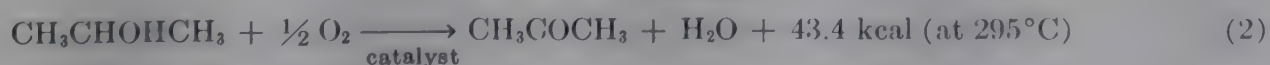
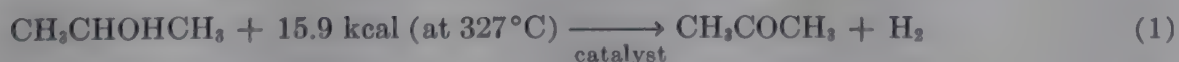


Figure 1.

Synthesis by Dehydrogenation of Isopropyl Alcohol. Acetone may be made from isopropyl alcohol (see Propyl alcohols) either by catalytic dehydrogenation (eq 1) or by catalytic oxidation (eq 2) (7).



The equilibrium of the dehydrogenation reaction is shifted in favor of acetone by increasing temperature. At 325°C, 97% conversion is theoretically possible. Catalysts include copper and its alloys and metal oxides and salts. In one commercial version, the catalyst is zinc oxide (7 to 8% on pumice carrier). Isopropyl alcohol is fed to the catalyst beds with an equimolar ratio of hydrogen to decrease catalyst fouling. At an operating temperature of 380°C, conversion starts at 98% per pass but drops to the point where catalyst regeneration is necessary after 10 days. At this point, organic material is burned off the catalyst using a mixture of 2% oxygen and 98% nitrogen at 500°C. Overall catalyst life is about six months.

The hot reactor effluent contains acetone, unconverted isopropyl alcohol, hydrogen, and minor amounts of by-products, such as propylene and diisopropyl ether. The mixture is cooled and the noncondensable gases are scrubbed with water. Because the resultant gas stream is mainly hydrogen, a part of it can be recycled to control catalyst fouling. The liquids are fractionally distilled taking concentrated acetone overhead and a mixture of isopropyl alcohol and water as bottoms. In a second fractionating column, the aqueous isopropyl alcohol is concentrated to the 91% constant-boiling mixture for recycle to the reactor. The water removed may be rejected or reused in the gas scrubber.

In the oxidation version of the process, the exothermic heat of reaction makes temperature control more critical. Isopropyl alcohol mixed with air is fed to reactors maintained at 400–600°C. Either copper or silver is used as catalyst. Reactor products are treated similarly to those from the straight dehydrogenation process.

Fermentation Process. Until the late 1930s, starch was the chief raw material used in the fermentation process for making butyl alcohol and acetone. Using cornstarch and the original Weizmann organism (*Clostridium acetobutylicum*), normal butyl alcohol, acetone, and ethyl alcohol are produced in a ratio of approximately 56:32:12. However, competitive factors led to the search for and discovery of strains which could ferment the less expensive raw material, molasses. In addition, some of these cultures raised the production of the more valuable butyl alcohol, giving ratios of butyl alcohol to acetone to ethyl alcohol of about 70:25:3. Since this discovery, molasses has been the preferred raw material for the fermentation process (9).

The process is divided into four steps: the building up of cultures, dilution and sterilization of the molasses, fermentation, and distillation. A pure stock culture of bacteria in spore form is added to a sterilized glucose medium. The spores are activated by heating and then allowed to grow at 87°F for a day. The culture is then transferred to a larger vessel containing a sterilized solution of molasses, ammonium sulfate, and buffers. Successive growth, testing, and transfer occur until the volume of culture is built up to 0.5 to 3% of the fermentation mix.

In the final fermentation, the molasses is diluted with water, and in some cases with recycle stillage, to give a concentration of about 6% sugar. It is then sterilized by steam injection, cooled to 87°F, and mixed with the previously prepared inoculum in a sterilized fermentation tank. Small amounts of nutrients containing nitrogen and phosphorus may be added to supplement those in the molasses. Ammonia is added both as an additional nutrient and to neutralize acidity.

The fermentation mix begins to evolve carbon dioxide and hydrogen shortly after inoculation. The pH is maintained above 5 but below 7 by adding the ammonia as needed. After 36 to 48 hours, the fermentation mix, containing about 2% solvents, is

steam-distilled in the “beer still.” The overhead is about 50% solvent which is fractionally distilled into normal butyl alcohol, acetone, and ethyl alcohol. The bottoms product (called distillation slop or stillage) contains proteins and vitamins such as riboflavin. It may be recycled to the fermentation or dried and sold as animal feed.

Normally, the yield of solvents is 28 to 33% by weight of the sugar charged. However, freedom from contamination is essential to maintain the yield and rate of fermentation. All feedstocks and equipment must be sterile and the inoculum free from lactic acid bacteria and bacteriophages.

Other Processes. Some acetone is made in other countries from acetylene via acetic acid. In addition, acetone has been made in Canada by a single-stage catalytic reaction of acetylene and steam (10).

Economic Aspects

In the United States, owing to the availability of large quantities of propylene, the only process used to produce acetone alone is the dehydrogenation of isopropyl alcohol. However, increasing amounts are being made as coproducts with other chemicals. Table 1 shows distribution of production in the United States, 1960 capacity, and prices. Particularly noteworthy is the rapid increase in production of acetone, as a coproduct with phenol, from cumene. Furthermore, production by oxidation of propane–butane mixtures is now greater than that by fermentation. The latest figure for production from isopropyl alcohol may include 50 to 100 million pounds of acetone made as a coproduct of hydrogen peroxide and glycerin synthesis.

Table 1. United States Acetone Production, Capacity, and Prices (11)

Acetone production, millions of pounds							
Year	From isopropyl alcohol	By fermentation	From cumene	From propane and butane oxidation	Total	Price, ¢/lb	
						Drums	Tanks
1945	307.4	42.4	0	0	349.8	8.00	7.00
1950	458.8	23.7	0		482.5	9.25	7.50
1955	434.8	27.4	40.4	36.2	538.8	9.00	7.00
1960	612.7	11.7	100.5	36.4	761.3	10.50	8.00
Capacity, millions of pounds							
1960	852	45	132	35	1064		

Table 2. Foreign Acetone Production, Millions of Pounds

Country	1954	1957	1958	1959	1960
Argentina (12)			2.2	2.8	
Brazil (13)				8.3	
France (14,15)		64.0	69.6	84.0	107.5
Great Britain (16)	97.7		113.6		
Italy (17)		9.3	8.4	10.8	
Japan ^a (18,19)			6.9	18.1	25.9
Spain (20)		2.6	2.7	2.6	2.6

^a Japanese statistics include only petrochemical production.

Table 2 gives acetone production figures for some foreign countries which manufacture substantial quantities. It is apparent that foreign production is rising rapidly.

United States capacity for acetone synthesis was considerably greater than production in 1960 and will probably continue to be so as new plants producing acetone as coproduct are built. This abundance of capacity will have a tendency to keep acetone prices at competitively low levels.

Analysis and Specifications

Acetone can be determined by treating with hydroxylamine hydrochloride and titrating the liberated hydrochloric acid (21). The formation of iodoform from the reaction of acetone with iodine is the basis of another useful method of analysis. The excess iodine is titrated, and the amount which has reacted with the acetone is thus determined by difference (22).

Commercial acetone as now produced is almost a chemically pure product. Its chief impurity is usually a few tenths of one percent of water. Acetone contains no oxidizable impurities, and on the addition of a few drops of permanganate, the color is retained for several hours. Acetone is shipped in ordinary steel tank cars or drums without causing corrosion, an indication of its freedom from impurities of an acidic nature. Owing to its low flash point, the red caution labels must be attached to all containers, whether tank cars or drums. The following specifications, which represent the average of the various producers, indicate the chemical purity of commercial acetone as now produced: purity, 99.5% by weight; distillation range, 1°C (55.8–56.8°C); specific gravity, 0.792 at 20°/20°; acidity, not more than 0.002% calculated as acetic acid; color, practically water-white; oxidizable impurities, pink color obtained by addition of 1 ml 0.1% solution of potassium permanganate to 100 ml acetone retained for at least 2 hours at 25°C; water content, fully miscible with 19 volumes of 60°Bé gasoline at 20°C; water solubility, completely miscible with distilled water.

Health and Safety Considerations

There have been no corroborated reports of ill effects of acetone on industrial workers other than skin irritations resulting from its defatting action. Maximum allowable concentration for prolonged exposure to vapors is 1000 parts per million in air (23). Acetone taken by mouth in doses of 15–20 grams daily for several days was shown by Albertoni to produce no bad effects other than a slight drowsiness. Kagan, in personal experiments, found it impossible to inhale concentrations of 8500 parts per million for longer than 5 minutes owing to acute irritation of the throat (24). In general, there seem to be no indications that acetone presents any hazards to workers who use it in rooms that are fairly well ventilated. Good ventilation is also desirable to prevent any possible hazard of fire due to the accumulation of acetone vapors.

Uses

The changing end-use pattern for acetone is shown in Table 3. It can be seen that the main trend is upward, but there are some marked variations in the individual-use categories.

Table 3. Estimated United States Acetone End-Use Patterns, 1947 to 1960

End use	1947 (25)		1951 (25)		1957 (26)		1960 (27)	
	Million pounds	%	Million pounds	%	Million pounds	%	Million pounds	%
cellulose acetate, solvent, and intermediate	190	48	155	28	63	10	40	5
other solvent uses								
acetylene	18	5	25	4	31	5	30	4
paint, varnish, and lacquer	36	9	40	7	68	10	75	10
miscellaneous	36	9	31	6	52	8	85	11
derivative solvents ^a								
methyl isobutyl ketone and 4-methyl-2-pentanol			154	28	205	31	235	31
others ^b			53	9	63	10	90	12
methyl methacrylate ^a			28	5	78	12	105	14
miscellaneous derivatives (bis-phenol A, acetyl acetone, drugs, vitamins, etc) ^a			40	7	84	13	90	12
exports (28)	37	9	34	6	7	1	11	1
totals (29)	397	100	560	100	651	100	761	100

^a The subtotal for all of these in 1947 is 80 million pounds or 20% of the total.

^b These include diacetone alcohol, mesityl oxide, hexylene glycol, isophorone, etc.

At one time, the largest use for acetone was in the production of cellulose acetate for fibers, photographic film, and plastics. Acetone was used both as a solvent (see Cellulose derivatives; Solvents, industrial) and to make acetic anhydride for acetylation of cellulose. However, starting in about 1951, acetone was displaced by other raw materials for acetic anhydride manufacture, and cellulose acetate production declined. As a result, acetone consumption for cellulose acetate dropped from first place to seventh among the use categories shown in Table 3.

Other solvent uses for acetone continue to maintain their relative standings among acetone uses. Because it is a powerful solvent for acetylene (qv), acetone is used to saturate absorbent packing in each acetylene cylinder so that excessive pressure can be avoided. It dissolves many natural gums and resins; most cellulose derivatives including nitrocellulose, cellulose esters, and ethyl cellulose; and many synthetic resins, such as vinyl and modified phenolic types, alkyds, and methacrylates. Many solvent formulations and removers for paints, varnishes, and lacquers include acetone as a fast-evaporating component. It is used as a solvent in smokeless powder manufacture, cements, artificial leather, and extraction processes of many kinds.

The largest use category for acetone is now in manufacture of derivative solvents, particularly methyl isobutyl ketone (see Ketones) and 4-methyl-2-pentanol (methylisobutylcarbinol) (see Alcohols, higher, synthetic). The initial step in making these two derivatives is the base-catalyzed aldol condensation of acetone to diacetone alcohol (see under Derivatives). Dehydration gives mesityl oxide, $(CH_3)_2C=CHCOCH_3$ (see Ketones), which may be hydrogenated in steps to methyl isobutyl ketone and methylisobutylcarbinol. Hydrogenation of diacetone alcohol yields 2-methyl-2,4-pentanediol or hexylene glycol (see Glycols). At elevated temperatures and with base catalysis, acetone may be condensed and dehydrated to isophorone (see under Derivatives), one of the strongest solvents for nitrocellulose.

A rapidly growing use for acetone is in the manufacture of methyl methacrylate (see Methacrylic compounds) via acetone cyanohydrin.

Among the miscellaneous derivatives, bisphenol A (see Alkylphenols) is a relative newcomer whose production for epoxy resins is increasing rapidly. This material is made by acid-catalyzed condensation of acetone with phenol (7). Other derivatives of acetone are used as drugs, vitamins, rubber additives, and cosmetics.

The export market for United States acetone has declined because of growing foreign self-sufficiency. Imports have been relatively insignificant.

Derivatives

Diacetone alcohol (4-hydroxy-4-methyl-2-pentanone), $\text{CH}_3\text{COCH}_2\text{C}(\text{OH})(\text{CH}_3)_2$, bp 166°C with decomposition back to acetone at atmospheric pressure; miscible with water, alcohol, and ether (30); prepared by base-catalyzed condensation of acetone, preferably in the liquid phase at about room temperature. Unconverted acetone is distilled off for recycle followed by vacuum distillation to recover the product (7). Diacetone alcohol is used as a high-boiling solvent and in hydraulic brake fluids.

Isophorone (3,5,5-trimethyl-2-cyclohexen-1-one), $\text{COCH}:\text{C}(\text{CH}_3)\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2$, bp 215.2°C ; fp -8.1°C ; insoluble in water (31); prepared by passing acetone over calcium oxide, hydroxide, or carbide, or mixtures of these at 350°C and atmospheric pressure; also prepared by heating acetone with aqueous alkali metal hydroxide at about 150°C under pressure and distilling to separate the unconverted acetone, diacetone alcohol, and mesityl oxide for recycle (7). Isophorone is a high-boiling solvent and an intermediate in the synthesis of 3,3,5-trimethylcyclohexanol and of 3,5-xyleneol.

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ACETONITRILE, CH_3CN . See Nitriles and isocyanides.

ACETONYLACETONE, $\text{CH}_3\text{CO}(\text{CH}_2)_2\text{COCH}_3$. See Ketones.

ACETOPHENETIDIN, $p\text{-CH}_3\text{CONHC}_6\text{H}_4\text{OC}_2\text{H}_5$. See Analgesics and antipyretics.

ACETOPHENONE

Acetophenone (methyl phenyl ketone, acetylbenzene), $\text{CH}_3\text{COC}_6\text{H}_5$, is an almost colorless, highly refractive, normally liquid ketone possessing a pleasant aromatic odor. In medicine and related fields it is usually called "hypnone" because of its use as a hypnotic. Acetophenone was first prepared by Friedel (1) in 1857 by distillation of a mixture of calcium benzoate and calcium acetate. In 1885 Dujardin-Beaumetz and Bardet discovered its powerful soporific properties, but, with the later discovery of better hypnotics, which have more positive action and are less toxic, acetophenone has been largely displaced for this purpose.

Acetophenone occurs naturally in oil of castoreum (2,3), oil of labdanum resin (4), and in the buds of balsam poplar (*Populus balsamifera*) (5). It is the major constituent of oil of *Stirlingia latifolia* (6). The heavy-oil fraction of coal tar contains small amounts of this ketone (7).

Properties

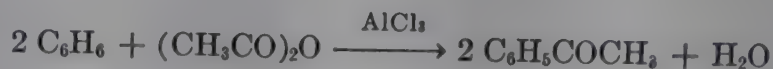
Constants. Fp, 19.655°C ; bp, 202.0°C ; bp_{10} , 78.8°C ; bp_1 , 39.0°C ; d_{25}^{25} , 1.0266; d_4^{20} , 1.0810; n_D^{20} , 1.5342; closed-cup flash point (Tag), 177°F ; insoluble in water, but miscible in all proportions with common organic solvents. Additional data are given in the bibliography (8–10).

Reactions. Acetophenone is a typical alkyl aryl ketone (see Ketones). Its reactions fall into three general classes: (a) reactions involving the carbonyl group, such as the addition of Grignard reagents and the condensation to dyprone, $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)=\text{CHCOC}_6\text{H}_5$ (acetophenone, however, does not form an addition compound with sodium bisulfite); (b) nuclear substitution, such as nitration to produce *m*-nitro-

acetophenone; and (c) side-chain substitution, such as bromination to produce α -bromoacetophenone.

Manufacture

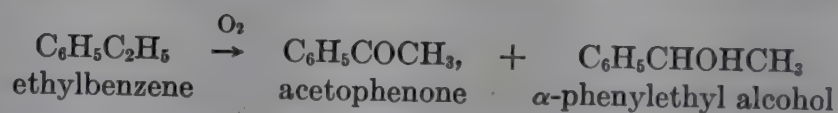
Acetophenone is produced by two processes, the oxidation of ethylbenzene with air and the peroxidation of cumene (isopropylbenzene) with air. Before 1949 the principal source was the Friedel-Crafts reaction of benzene, aluminum chloride, and acetic anhydride.



(See Friedel-Crafts reaction.) The oxidation of ethylbenzene replaced this process until 1956 when acetophenone also became available from the cumene peroxidation process.

From Ethylbenzene (9,11). Ethylbenzene is manufactured by alkylation of benzene with ethylene (see Alkylation; Styrene and styrene polymers; Xylenes and ethylbenzene). The oxidation of ethylbenzene is carried out in two acidproof, brick-lined reactors in series. Ethylbenzene and manganese acetate catalyst (15% aqueous solution) are fed into the top of the first reactor and air is dispersed in the liquid at the bottom. Liquid from the bottom of the first reactor is pumped to the top of the second reactor and more air is added at the bottom. In both reactors the temperature is 126°C and the pressure 30 psi. Total contact time between ethylbenzene and air is about 1.5 hours.

About 16% of the ethylbenzene is oxidized in the first reactor and an additional 10% in the second. Eighty-eight percent of the ethylbenzene that reacts forms acetophenone (2 parts) and α -phenylethyl alcohol (phenylmethylethanol)(1 part).



The remainder is oxidized to acids (including benzoic acid) and residue. The product is treated with 10% aqueous sodium hydroxide to extract acids and precipitate the manganese catalyst. Distillation of the organic layer yields ethylbenzene, which is recycled, and a mixture of acetophenone (68%) and α -phenylethyl alcohol (32%). This is dehydrogenated at 200°C in the presence of a catalyst with a stream of nitrogen flowing through the reactor to remove hydrogen. A mixture containing 80% acetophenone, 6% α -phenylethyl alcohol, and 14% ethylbenzene is produced. Purified acetophenone is obtained by distillation. Purity control is achieved by controlling the freezing point of the distillate which is bulked to give a product with a minimum freezing point of 18.3°C.

The overall yield of acetophenone is 85% on ethylbenzene consumed. The following quantities of utilities are required to produce one pound of acetophenone: 0.04 kilowatt of electricity, 0.32 cubic foot of fuel gas, 27 gallons of river water, 7.0 pounds of steam, and 14.3 cubic feet of compressed air.

During World War II styrene was produced from ethylbenzene via acetophenone and α -phenylethyl alcohol. This mixture was hydrogenated to convert the acetophenone to α -phenylethyl alcohol and the alcohol was dehydrated over titania catalyst to styrene. This process was used by Carbide and Carbon Chemicals Co. at Institute, West Virginia.

From Cumene (qv) (12-14). Acetophenone is also available as a by-product from the peroxidation of cumene to produce phenol (qv) and acetone (qv). Cumene is made by alkylating benzene with propylene. A mixture of cumene, water, soda ash emulsifier, and cumene hydroperoxide as an oxidation initiator is brought into contact with air at 130°C until 35 to 50% of the cumene is oxidized to cumene hydroperoxide. The ratio of water to oil is between 2:1 and 5:1 and the pH is controlled between 8.5 and 10.5.

Crude cumene hydroperoxide is fed into an acidifier containing 10% sulfuric acid at 80-120°C and close to atmospheric pressure. The main reaction is as follows:



A mixture of the following approximate composition is obtained: 9.1% acetone; 15.2% phenol; 0.8% acetophenone; 1.5% α -methylstyrene; and 73.4% cumene. The product is separated by distillation or by a combination of distillation and extraction. Acetone is distilled off first and then the cumene, which is recycled after purification to remove a small amount of α -methylstyrene. This leaves a mixture of phenol and acetophenone which is separated by distillation or solvent extraction. One process employs butyl acetate which selectively extracts phenols. Butyl acetate and phenol are easily separated by distillation. Acetophenone is recovered from the raffinate.

The capacity of the cumene peroxidation plants in the United States is about 220 million pounds of phenol per year. Approximately 11 million pounds of acetophenone per year would be made at capacity operation. There are four companies in the United States that operate cumene peroxidation plants: Standard Oil Co. of California; Allied Chemical Corp.; Hercules Powder Co.; and Shell Chemical Corp. Monsanto Chemical Co. (as of 1962) is constructing a plant to produce 75 million pounds of phenol per year.

Standards and Containers. The perfumery grade meets the following specifications: ketone, 98% minimum by titration with hydroxylamine (15); d_{25}^{25} , 1.025-1.028; congealing point, 19.0°C, minimum; chlorine (Beilstein flame test), free; color, water-white; odor, clean floral character, free of any secondary odors. The technical grade meets the following specifications: ketone, 97% minimum; d_{20}^{20} , 1.027-1.031; freezing point, 18.3°C, minimum; boiling range (760 mm), 194-206°C. Acetophenone is available in bottles, cans, 55-gallon drums, tank cars, and trucks.

Industrial Hazards. Although acetophenone has been used as a hypnotic, there are no unusual hazards involved in its manufacture and handling. The Tag closed cup flash point is 177°C. There are no special regulations governing shipping. Its freight description is Chemicals, NOIBN. The LD_{50} for rats is 3 grams per kilogram.

Economic Aspects. The United States production is estimated to be one million pounds annually as of 1962. About half is made from ethylbenzene and the other half from cumene. Much larger quantities could be made available as by-product from cumene peroxidation. Production has steadily increased since 1930 when it was first made in significant quantities in the United States. In 1941, 27,000 pounds were produced; in 1951 production was about 350,000 pounds.

Technical-grade acetophenone is available in tank cars at about \$0.30 per pound. Smaller quantities are quoted slightly higher. Perfumery grades sell for \$0.65 to \$0.85 per pound. The price of acetophenone has declined steadily as its use expanded and as it became available from large-scale chemical operations. In 1939 it sold for

\$1.05 per pound and in 1953 for \$0.75 per pound. During World War II the price rose to about \$1.70 per pound.

Uses and Applications. Acetophenone is used as a process solvent, a perfume ingredient, and as an intermediate for the synthesis of pharmaceuticals, resins, corrosion inhibitors, rubber chemicals, and dyestuffs. As a solvent its high boiling point, pleasant odor, and stability are important advantages. It serves as a solvent for cellulose ethers, esters, and resins, and also as a plasticizer (see Plasticizers; Solvents, industrial). Acetophenone is used as a major constituent of new-mown hay and hawthorn types of perfumes (qv); it is also used for honeysuckle and jasmine types and for flavoring tobacco.

Derivatives

***p*-Methylacetophenone** (methyl *p*-tolyl ketone), $\text{CH}_3\text{COC}_6\text{H}_4\text{CH}_3$, formula weight 134.08, is a colorless, highly refractive liquid having a pronounced aromatic odor; mp, -23°C ; bp, 227°C ; b_{11} , 112.5°C ; d_{25}^{25} , 1.002; n_D^{20} , 1.5335. It is made by a process similar to that for acetophenone, but from toluene instead of benzene (16–20). It can also be made by oxidation of *p*-cymene (21). The chief use for *p*-methylacetophenone is in perfumery as a mimosa base and in place of acetophenone in more expensive perfumes.

α -Bromoacetophenone (bromacetophenone, phenacyl bromide), $\text{BrCH}_2\text{COC}_6\text{H}_5$, formula weight 199.05, forms white, rhombic prisms and is a lacrimatory compound obtained by bromination of acetophenone; mp, 50°C ; b_{12} , 140°C ; d_4^{20} , 1.647. It is employed in organic synthesis and in the manufacture of dyes and has limited military use (see Chemical warfare).

α -Chloroacetophenone (chloracetophenone, phenacyl chloride), $\text{ClCH}_2\text{COC}_6\text{H}_5$, formula weight 154.59, forms white, rhombic crystals and is a lacrimatory compound made from benzene and chloroacetyl chloride by a Friedel-Crafts reaction; mp, 59°C ; bp, 247°C ; b_{14} , 140°C ; d_4^{15} , 1.324. It may also be made by chlorination of acetophenone. In addition to being a lacrimator, it is a respiratory and skin irritant, and is used as a "tear gas" (see Chemical warfare). It is also an official denaturant for industrial alcohol (see Ethanol).

***p*-Methoxyacetophenone** (acetanisole, methyl *p*-anisyl ketone), $\text{CH}_3\text{OC}_6\text{H}_4\text{COCH}_3$, formula weight 150.17, forms white, crystalline plates having a mild aromatic odor suggestive of methylacetophenone and coumarin. It is not prepared from acetophenone, but is synthesized from anisole, $\text{C}_6\text{H}_5\text{OCH}_3$, and acetic anhydride by the Friedel-Crafts reaction; mp, $38\text{--}39^\circ\text{C}$; bp, 258°C ; d_4^{41} , 1.0818; congealing point, 36.5°C . *p*-Methoxyacetophenone is not a widely used synthetic, but it does have value in Oriental bouquets, new-mown hay, and fougère types of perfumes. It is also used in soap perfumery. Production in 1959 was 8000 pounds.

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ACETYL CHLORIDE, CH_3COCl . See Acetic acid derivatives.

ACETYLENE

Acetylene (ethyne, IUPAC), a colorless gas of formula C_2H_2 , or $\text{HC}\equiv\text{CH}$, molecular weight 26.04, was discovered and identified by Edmond Dave in 1836. The discovery by Morehead and Willson in 1892 of the electric furnace process for preparing calcium carbide made acetylene easily and economically available. The gas became one of the major raw materials of the chemical industry and had its most significant growth period starting around 1930. The present-day large-scale use of acetylene as the principal building block for the synthesis of many commercially important products is based on the high reactivity which the triple bond imparts to the compound. In addition, air-acetylene and oxyacetylene flames are widely used for metalworking.

The oldest, but nevertheless the most widely used, method for the generation of acetylene is the reaction of water with calcium carbide. However, the manufacture of acetylene from hydrocarbons is growing steadily and large-scale facilities using various hydrocarbon processes are now in operation in the United States and Europe.

Physical and Chemical Properties

Acetylene freezes at -81°C . Its vapor pressure at this point is a little above atmospheric (18 psig). The sublimation point of acetylene is -83.4°C at atmospheric pressure; bp, -75°C at 1.68 atm; triple point on phase diagram, -82°C and 1.2 atm (915 mm Hg); latent heat of vaporization, 264 Btu/lb or 3815 gcal/gram-mole at the triple point; crit temp, 36.3°C ; crit pressure, 61.6 atm or 892 psig; crit vol, 113 cm^3 /gram-mole; crit density, 0.23 g/cm^3 ; sp heat at constant pressure, c_p (room

temp), 0.402 Btu/lb; molar heat of combustion, 312.4 kcal at constant pressure. One liter of acetylene weighs 1.1709 g at 0°C and 760 mm Hg (STP).

Acetylene is highly soluble in a number of organic solvents. It is also soluble in water, which at 0°C dissolves 1.7 times and at 15.5°C 1.1 times its own volume of acetylene. The solubility of acetylene in various selective solvents used for its storage, purification, and separation from pyrolysis gas mixtures is indicated in Table 1.

Table 1. Solubility of Acetylene in Selective Solvents

Solvent	Bp, °C	Acetylene solubility ^a
butyrolactone	204	11.8
acetone	56.5	20.8
dimethylformamide	153	31.4
<i>N</i> -methylpyrrolidone	202	34
ammonia	-33.35	34.1

^a Volumes of acetylene (STP) per volume of solvent at 25°C and acetylene partial pressure of one atmosphere.

Acetylene forms a solid hydrate, $C_2H_2 \cdot 6H_2O$. The hydrate decomposes at -15.4°C under atmospheric pressure and at 0°C develops a vapor pressure of 5.7 atmospheres. The critical decomposition point, where the vapor pressure curve of the hydrate intersects the vapor pressure curve of acetylene (saturated with water), is 16°C. The heat of formation of the hydrate at 0°C is 15.41 kcal (1,2).

Acetylene is a highly endothermic compound with a heat of formation of -54.9 kcal/gram-mole (3800 Btu/lb). It is thermodynamically unstable at room temperature and can be decomposed into its elements even in the absence of oxygen with the liberation of its heat of formation. The thermal decomposition of acetylene can proceed so rapidly that explosions and detonations may result, depending on the kind of ignition and conditions of temperature, pressure, and size of the containing vessel. Acetylene in liquid or solid form can be made to detonate. Although at temperatures near the freezing point decomposition of either form is not easily initiated by heat, impact, or friction, exposure to a fusing wire will result in violent explosions at temperatures approaching room temperature.

Acetylene burns in air with a high flame temperature. The temperature of the oxyacetylene flame is one of the highest for any mixture of gases and is variously reported as 5400 to 6300°F.

Many of the uses of acetylene in syntheses are based on four fundamental reactions which are more or less generally applicable: vinylation (introduction of the vinyl group, $CH_2=CH-$); carbonylation (see page 206); polymerization; and ethynylation (introduction of the ethynyl group, $HC\equiv C-$) (3).

The high chemical reactivity of acetylene, which is based on its triple bond and its high endothermic heat of formation, makes it a chemical of extreme versatility in industrial syntheses. Therefore, many of the reactions of acetylene are discussed under Uses; a few others may be mentioned here.

Haloacetylenes. Dihalogenated acetylenes can be obtained by reaction with a hypohalous salt.



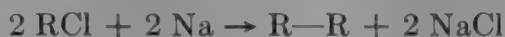
Monohalogenated acetylenes can only be obtained by indirect procedures, such as the decarboxylation of halogenated propiolic acid,



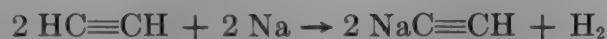
or the reaction of dihaloethylene with alcoholic caustic potash,



The haloacetylenes do not give the characteristic substitution reactions of alkyl or aryl halides, such as



Metal Derivatives. Either one or both of the methine hydrogens ($\equiv\text{CH}$) of acetylene can be replaced by certain metals to form acetylides. The acetylides are useful in chemical synthesis either as intermediates or catalysts for the reaction of acetylene with a variety of organic compounds. They are highly explosive when dry and decompose to yield acetylene on treatment with water or dilute mineral acids.



Acetylene reacts with sodium or sodamide in liquid ammonia to give monosodium acetylide which can be converted to disodium acetylide by heating in a vacuum at 200–400°C. Potassium and lithium also form acetylides. Copper, silver, and mercury acetylides are formed by passing acetylene into ammoniacal solutions of their salts. However, gold does not form an acetylide.

Certain carbides, such as calcium carbide, can be considered to be acetylides since they yield acetylene on treatment with water. However, magnesium carbide is unusual in that it yields 2-propyne (methylacetylene) on reaction with water.

Other metal derivatives of value in synthesis are the acetylenic Grignard reagents. These are obtained by a metathetical interaction of acetylene with an alkylmagnesium bromide in an inert solvent. Acetylene normally yields the dimagnesium bromide ($\text{Br}-\text{Mg}-\text{C}\equiv\text{C}-\text{Mg}-\text{Br}$), but the monomagnesium bromide ($\text{HC}\equiv\text{C}-\text{Mg}-\text{Br}$) can be prepared under carefully controlled conditions.

Self-Addition. The important reaction leading to vinylacetylene is described under Uses.

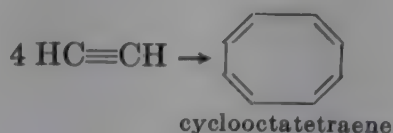


Many other self-addition reactions are possible with acetylene.

Benzene, together with other aromatics, is obtained by passing acetylene through a heated zone (600–700°C) in the presence of iron, silicon, or other heavy metals. However, Reppe found that with complexes of triphenylphosphine and nickel halides or nickel carbonyl as catalysts, acetylene was converted under mild conditions to a product consisting of 88% benzene and 12% styrene.



Undoubtedly, the most fascinating development in this phase of acetylene chemistry was Reppe's discovery that acetylene could be polymerized to give the cyclopolyolefin, *cyclooctatetraene*.



The cyclopolymerization is carried out in tetrahydrofuran at 60–70°C and 10–25 atm acetylene pressure with anhydrous nickel cyanide as the catalyst. In addition to cyclooctatetraene, the reaction product contains vinyl cyclooctatetraene, 1-phenyl-*cis*-1,3-butadiene, azulene, and benzene.

Manufacture from Calcium Carbide

The generation of acetylene is accomplished by the reaction between water and calcium carbide, $\text{CaC}_2 + 2\text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + \text{C}_2\text{H}_2 + 32 \text{ kcal/mole}$ (900 Btu/lb of carbide).

The most important consideration in the design of industrial acetylene-generating processes is the avoidance of high temperatures and high pressures within the generating equipment. The heat of reaction must be rapidly and efficiently dissipated in order to avoid local overheating of calcium carbide which, in the absence of sufficient water, may become incandescent and initiate explosive decomposition of the gas in the generating vessel. As a rule, the temperature in the generators is maintained below 300°F to minimize the polymerization of acetylene and other side reactions which may form contaminating by-products. For protection from dangerously high pressures, industrial acetylene gas generators are equipped with relief valves which maintain the pressure within the equipment below 15 psig. This figure is commonly accepted as a safe upper limit for the operating pressure.

Most carbide acetylene processes are "wet" processes, in which the hydrated lime by-product is obtained in the form of a slurry or a thin liquid suspension in water. During operation of the generator the slurry is maintained in suspension by means of a mechanical agitator and is intermittently removed. The hydrated lime is usually permitted to settle out in a pond where the liquid is separated from the solids. The wet solids are marketed for the neutralization of acid wastes, as a fertilizer or soil conditioner, as a whitewash, or as a mortar constituent. The hydrated lime may also be processed to calcium oxide and recycled in the form of briquets to produce calcium carbide (4).

The three principal methods for generating acetylene from calcium carbide are carbide-to-water generation, water-to-carbide generation, and dry generation.

Carbide-to-Water Generation. This batchwise process is the one most widely used in the United States. Generally accepted standards for the design and construction of generating equipment using this technique have been developed by the Underwriter's Laboratories, Inc. One gallon of water capacity is provided per pound of carbide and a gas-generating rate of one cubic foot per hour per pound of carbide hopper capacity is considered normal. There are, however, stationary "double-rated" generators available with a rate of two cubic feet per hour per pound of carbide hopper capacity. The latter equipment must pass certain tests prescribed by regulating bodies to assure safety of operation at the increased load.

There are two classes of carbide-to-water generators. One class comprises the low-pressure generators, which operate at pressures below 1 psig, and the other one, the so-called medium-pressure generators, which employ pressures between 1 and 15 psig.

There are numerous variations in the design of commercially available carbide-to-water generators. However, the basic design of these units is practically identical and consists of a cylindrical, vertical vessel, filled with water, which supports an upper housing. The water vessel is equipped with means for filling and draining and, in most cases, with a manual agitator for keeping the hydrated lime in suspension during generation. The upper housing, which contains the carbide hopper and the carbide feed system, is equipped with one or more pressure gages and relief valves and a valved gas outlet line (see Figure 1). In order to protect the generators against flashbacks, originating from the acetylene-consuming equipment or from reverse-flow of oxygen from oxyacetylene equipment, hydraulic back-pressure valves are employed. In most cases, the generators are equipped with a mechanical interference mechanism, which, for safety reasons, enforces a prescribed sequence of operating procedures for the operator using the equipment.

The control of the rate of feed of the carbide into the water is important and is accomplished in numerous ways. In one method, which is used in medium-pressure generators, the gravity flow of properly sized carbide from the hoppers into the water shell is controlled by a valve which is actuated by a spring-operated rubber diaphragm. The motion of the diaphragm, which reflects the change of internal pressure in the generator, is transmitted to the valve which, in turn, either opens or closes with decreasing or increasing acetylene pressure.

The operating pressure in the generator is fixed by the compression of the control spring, which is located on the atmospheric side of the diaphragm, and opposes the internal force which tends to push the diaphragm outward.

A schematic drawing of a modern carbide-to-water acetylene generator is given in Figure 1. This generator operates under 13 psig pressure and is designed for continuous service without interruption for charging.

Another method of feeding carbide into water employs a revolving disc-and-plow mechanism, powered by a weight motor. The carbide is gravity-fed onto the disc and is pushed off the disc by a plow into the water. The speed of the rotating disc, and hence the rate of carbide feed, is controlled by a pressure-sensitive braking device.

Generators designed for operation at a constant rate usually employ a screw conveyor arrangement for moving carbide from the hopper into the water shell.

Carbide of proper size is important for the trouble-free operation of carbide-to-water generators. Medium-pressure automatic generators are designed to operate on a specified-size grade of carbide, such as 14 ND or $\frac{1}{4} \times \frac{1}{12}$ in. Low-pressure generators are frequently designed to operate with more than one size of carbide (see Calcium carbide under Carbides). Medium-pressure gravity feed generators and generators with revolving disc-and-plow mechanism are generally not operated with dust carbide.

Carbide-to-water generators show a very noticeable temperature rise during the course of normal operation. In properly designed and operating units, employing the recommended amount of water (one gallon of water per pound of carbide capacity), the temperature rises about 70–80°F in continuous operation at rated capacity. Thus, a generator, originally filled with 60°F water and operated at the rated capacity, will be ready for recharging after 4½ hours and its temperature will be about 135°F.

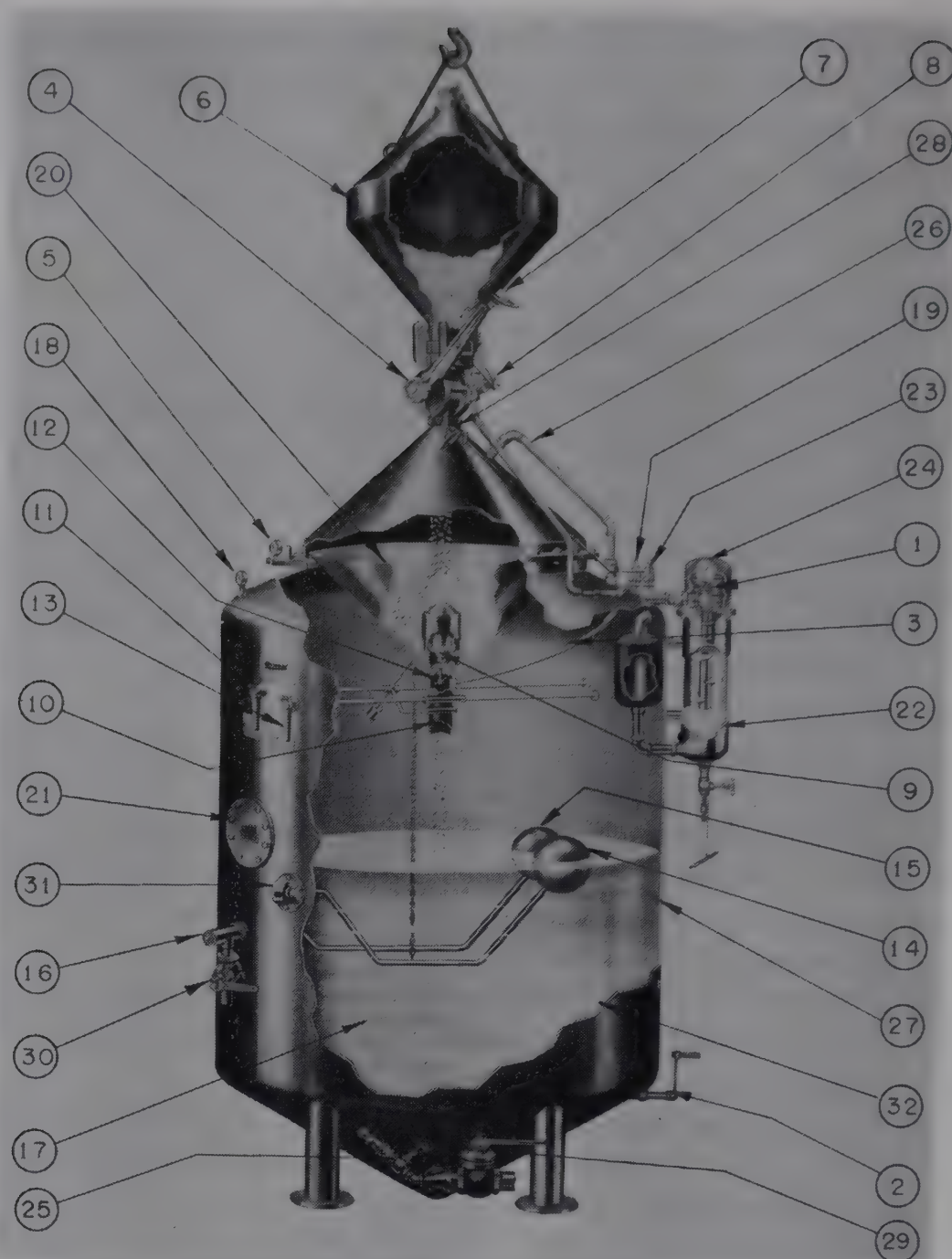


Fig. 1. Carbide-to-water acetylene generator. Courtesy Linde Company, Division of Union Carbide Corporation.

- | | |
|--|--|
| 1. Acetylene filter | 17. Generating chamber |
| 2. Agitator | 18. Generating-chamber pressure gage |
| 3. Atmospheric vent line | 19. Generating-chamber relief valve |
| 4. Carbide charging valve | 20. Generator hopper |
| 5. Carbide contents indicator | 21. Handhole cover |
| 6. Charging hopper | 22. Hydraulic back-pressure valve |
| 7. Charging-hopper pressure gage | 23. Hydraulic back-pressure valve—relief valve |
| 8. Charging-hopper vent valve | 24. Line pressure gage |
| 9. Feed control unit | 25. Low-level water fill valve |
| 10. Feed tube | 26. Pressure equalizing line |
| 11. Feed tube handle | 27. "Refill" level reference marker |
| 12. Feed valve | 28. Relief-valve trip mechanism |
| 13. Feed valve handle | 29. Residue drain valve |
| 14. Float, water level indicator and feed tube | 30. Water fill valve |
| 15. Float, water shutoff valve | 31. Water level indicator |
| 16. Float-operated water shutoff valve | 32. Water shell |

Water-to-Carbide Generation. This method, which has found only limited acceptance in the United States and Canada, has been used frequently in Europe. In this method, the rate of generation is simply regulated by the rate of water flow to the generator; hence, local undesirable hot spots may result, which may lead to hazardous overheating of the carbide mass and to the formation of polymers and other undesirable by-products. Water-to-carbide generation is generally used in small-size generators, such as in portable lamps, where the rate of generation and the heat of reaction are low and the mass of carbide involved is small.

Dry Generation. This water-to-carbide method, used in certain large-scale installations, has the advantage of being continuous and produces dry by-product lime which can be marketed as such or recycled to produce calcium carbide.

The dry process uses only about one pound of water per pound of carbide. Most of the heat of reaction is dissipated by vaporization of water. The reaction mass of dry lime and unreacted carbide must be continuously agitated to prevent hazardous localized overheating and formation of undesirable by-products. The acetylene is mechanically filtered to remove entrained lime dust. The lime is removed mechanically in a manner which prevents the escape of the gas.

Purification of Carbide Acetylene. The purity of carbide acetylene depends largely on the quality of the carbide employed and, to a much lesser degree, on the type and operation of the generator. Depending on the quality of the coke and lime used for the manufacture of the calcium carbide, a number of impurities are present in crude carbide acetylene. The nature and the amounts of the impurities in carbide acetylene are tabulated in Table 2.

Table 2. Impurities in Carbide Acetylene

Type	Amount, approx
phosphine	a few hundred ppm
divinyl sulfide	100 ppm (as H ₂ S)
ammonia	a few hundred ppm
oxygen	250 ppm or less
nitrogen	few tenths of a percent (<1.0)
arsine	3 ppm or less
methane, carbon dioxide, carbon monoxide, hydrogen	a few hundred ppm
silicon hydride (silane)	10 ppm or less
vinylacetylene	50 ppm
divinylacetylene	50 ppm
diacetylene	a few hundred ppm
propadiene (CH ₂ =C=CH ₂), hexadiene, buta- dienyl, acetylene, methylacetylene	traces (variable according to carbide quality)

The total amount of impurities in acetylene, apart from water, manufactured from a standard U.S. grade of carbide, is generally less than 0.4%.

Purification of acetylene involves in principle the oxidation and hydration of phosphine to phosphoric acid, the neutralization and absorption of ammonia, and the oxidation of hydrogen sulfide and organic sulfur compounds. Depending on the type and amount of impurities, and on the end use of the gas, numerous agents and processes

are employed. These range from simply passing the gas over purifying media to multistep chemical treatments, and can be conducted as dry or wet processes.

The most commonly used dry methods employ oxidizing agents, such as chromic acid or chromates, hypochlorite, permanganate, and ferric salts, deposited on solid carriers, such as diatomaceous earth, arranged in beds or layers through which the gas is passed at ambient temperature. Some of the purifying media can be regenerated several times with diminishing effectiveness until they eventually lose their activity. Because of the high material and labor requirements, dry purification of acetylene is not practiced in the chemical industry where large volumes of gas have to be treated.

Large-scale acetylene installations exclusively employ continuous, wet purification processes. Elaborate purification methods have been developed in Europe, where on certain locations relatively low-grade carbide is used to generate acetylene of a lesser purity. Continuous purification processes are then employed whereby the gas is contacted in successive steps with water, dilute caustic solution, and chlorine-water or hypochlorite solution, followed in certain locations by a final treatment with activated carbon (5-7). Such an intensive purification of acetylene is also beneficial in cases where the gas is to be used in processes employing sensitive catalytic systems.

The chlorine-water purification is particularly effective on organic sulfur compounds. The chlorine concentration (about 1.3 g of chlorine per liter of solution) is rather critical; concentrations of less than one gram per liter are said to be of little effect, and concentrations of more than two grams of chlorine per liter lead to explosions due to the formation of monochloroacetylene. Due to the presence of hypochlorous acid ($\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCl} + \text{HOCl}$), the action of this solution is mostly oxidative although undesirable chlorination side reactions cannot be entirely prevented. Small amounts of chloroform and tetrachlorodiethyl sulfoxide have been identified as by-products.

Manufacture from Hydrocarbons

Development of the modern processes for the manufacture of acetylene from hydrocarbons began in the 1920s when Badische Anilin- und Soda-Fabrik (BASF) initiated an intensive research program, based on Berthelot's early (1860) laboratory investigations on the conversion of low-molecular aliphatic hydrocarbons to acetylene by means of thermal cracking. BASF's development of the electric arc process led to the first commercial plant for the manufacture of acetylene from hydrocarbons. This plant was put into operation at Chemische Werke Huels in Germany in 1940. In the United States commercial manufacture of acetylene from hydrocarbons began in the early 1950s and is expanding rapidly. It has been estimated that, in the U.S., the 1963 hydrocarbon-acetylene capacity may increase to more than 700 million pounds per year compared with an estimated 1963 capacity of about 1125 million pounds per year of carbide-acetylene (8). All hydrocarbon-acetylene processes in operation or under development are thermal processes and differ essentially only in the manner in which the necessary energy for the reaction is supplied.

The method of producing acetylene by the thermal cracking of hydrocarbons takes advantage of the fact that, in contrast to the behavior of other hydrocarbons, the free energy of acetylene decreases at higher temperatures. At 1600°K or higher, acetylene is more stable than any other hydrocarbon. But even at these high temperatures, acetylene is less stable than its free elements and hence, the contact time at

this elevated temperature must be short in order to preserve the acetylene formed in the cracking process. This is the basis for all hydrocarbon-acetylene processes.

Thermodynamics and Kinetics. The principal conditions which must be considered in connection with the thermal method for the production of hydrocarbon-acetylene can be summarized as follows:

(a) The amount of energy required to convert hydrocarbons to acetylene is very large and must be applied at high temperatures to achieve a favorable free energy relation. For paraffinic feedstocks, the heat of formation for a gram atom carbon in acetylene decreases with the increasing length of the chain and it increases in the case of olefinic hydrocarbons. The heat of formation is of the order of magnitude required for the dissociation of steam.

The fundamental reaction involved in the case of methane (at 1250°C) can be expressed by the equation, $2\text{CH}_4 + 174,000 \text{ Btu} \rightarrow \text{C}_2\text{H}_2 + 3\text{H}_2$.

(b) The formation of acetylene begins at a relatively high temperature; in the case of methane, for example, this temperature is around 1500°K. The temperature required decreases with the increase in the number of carbon atoms of the hydrocarbon feed.

(c) The decomposition of hydrocarbons to carbon and hydrogen begins at relatively low temperatures. In the case of methane, for example, this occurs at 850°K. Hence, the decomposition into the elements proceeds in competition with the formation of acetylene. However, the rate of acetylene formation is greater than that of the decomposition reaction.

For the successful manufacture of acetylene from hydrocarbons it is necessary that the following process conditions be achieved: The hydrocarbon feed must be subjected to considerable amounts of energy at relatively high temperatures (above 1250°K) in the shortest possible time and then the attained equilibrium must be immediately quenched to about 550°K in order to preserve the acetylene formed. The time interval for the reaction should be of the order of milliseconds.

Some of the thermodynamic data related to the hydrocarbon-to-acetylene reaction are illustrated in Table 3 and Figure 2. Table 3 shows the heat of formation of various hydrocarbons divided by the number of carbon atoms in each hydrocarbon. The energy required to convert any of the hydrocarbons to acetylene may be obtained by taking the difference in energy value between acetylene and the hydrocarbon and

Table 3. Heats of Formation of Several Hydrocarbons

Hydrocarbon	Heat of formation, $-\Delta Q$, kcal/carbon atom at 1500°K
methane	-22.06
ethane	-12.87
<i>n</i> -butane	-9.28
<i>n</i> -octane	-7.53
carbon (solid)	0
hydrogen gas	0
benzene	+2.40
ethylene	+4.31
allylene (propyne, methylacetylene)	+13.62
allene (propadiene)	+14.23
acetylene	+26.27

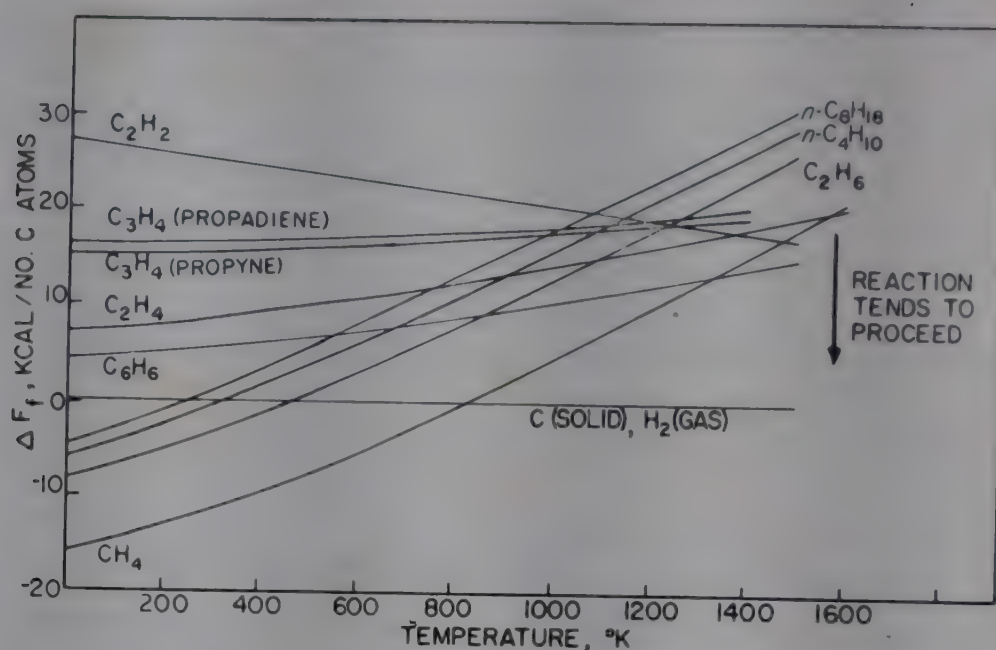


Fig. 2. Free energy of formation of several hydrocarbons.

multiplying by 2. Figure 2 indicates the favorable free energy relations existing in the temperature range under consideration. In Figure 2 the free energies of formation of hydrocarbons are plotted, divided by the number of carbon atoms in the molecule. The curves also indicate that the temperature required for the formation of acetylene decreases with an increase in the molecular weight of the paraffinic hydrocarbon and that, under most of the temperature conditions plotted, most of the hydrocarbons can decompose to the elements.

A decrease of the partial pressure of the hydrocarbons in the cracking system decreases the temperature required for the formation of acetylene. This has been accomplished in part by operation under reduced pressure or by employing a diluent such as steam with the hydrocarbons. In the case of steam, undesirable reactions may occur leading to the production of hydrogen and carbon monoxide. Nonreactive diluents lack the advantage of condensability possessed by steam. This results in lower acetylene concentrations in the reaction gas and more troublesome product recovery. The use of hydrogen as a diluent may offer certain advantages, even though the acetylene concentration in the reaction gas at the optimum dilution ratio is low (9,10).

Processes for the Manufacture of Acetylene from Hydrocarbons

It is not feasible to supply the necessary thermal energy by conducting heat through the walls of a vessel. Therefore, different approaches have been developed. These processes for manufacturing acetylene from hydrocarbons can thus be classified according to the means of supplying the thermal energy: electric discharge processes, regenerative furnace processes, and one-stage or two-stage partial combustion processes.

ELECTRIC DISCHARGE PROCESSES

The electric discharge processes have the advantages that the necessary energy can be supplied very rapidly and that the conversion of the hydrocarbons to acetylene can be appreciably higher than in regenerative or in partial combustion processes. The electric arc provides energy at a very high flux density so that the reaction time can be kept at a minimum.

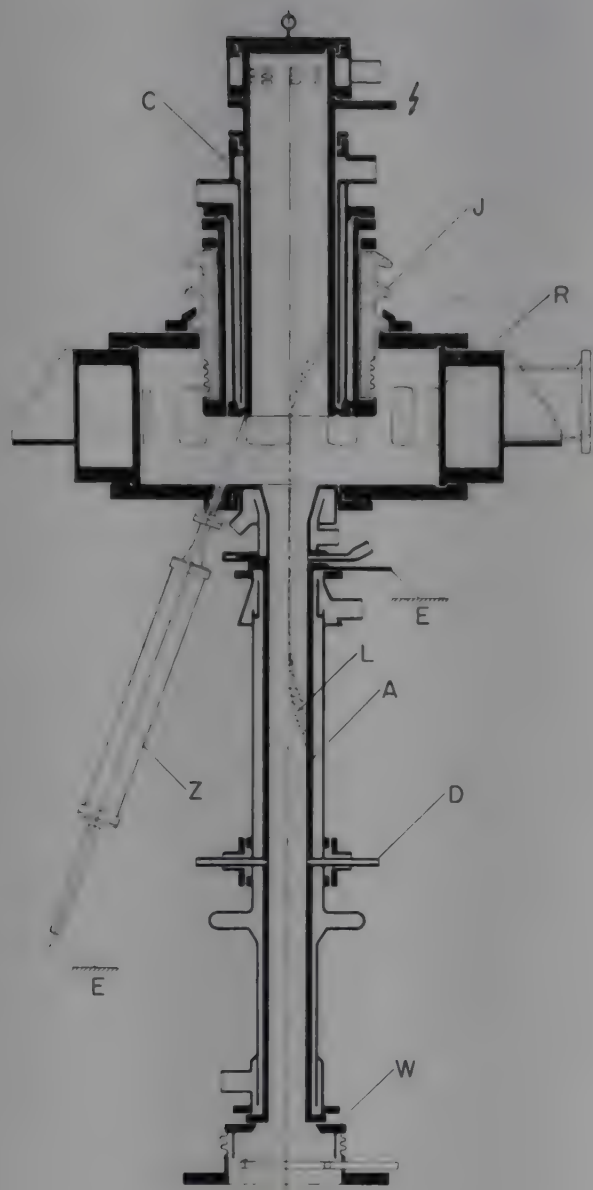


Fig. 3. Schematic drawing of a Huels arc furnace. Courtesy Chemische Werke Huels.

The electric arc process as practiced at the plant of Chemische Werke Huels, Germany, is at present the only electrical process in commercial operation (11). However, Du Pont is at present (1962) building an acetylene-from-hydrocarbon unit at Montague, Michigan, with a capacity of more than 50 million pounds per year. The plant is scheduled for completion in 1963 and will use a modified arc technique (12).

The Huels installation includes seventeen sets of arcs and has a capacity of 100,000 metric tons of purified acetylene per year. In addition, 55,000 metric tons of pure ethylene and $360 \times 10^6 \text{ m}^3$ hydrogen are produced as by-products. Each set has two arcs, which are used alternately in order to allow the replacement of electrodes, cleaning, and repair. The arcs use direct current supplied independently to each set by means of grid-controlled, mercury arc rectifiers.

Figure 3 shows the latest design of the Huels arc furnace. The gaseous feedstock enters the furnace tangentially through a turbulence chamber, R, and then passes with a rotary motion through pipe A (length approximately 1.5 m, diameter 85–105 mm). The arc, L, burns between the bell-shaped cathode, C, and the anode pipe, A (grounded at E). Due to the rotary motion of the gas passing through, the starting points of the arc rotate within the hollow electrodes. The cathodic or anodic starting point of the arc can move upward or downward freely. With the exception of the insulator, J, all parts of the furnace are made of iron. The wall thickness of the electrodes is 10–20 mm.

The arc is about 100 cm long and extends about 40–50 cm into the anode pipe. About 20 cm below the anodic starting point of the arc, cold hydrocarbons ($C \geq 2$) are introduced into the tube through several nozzles, K, to prequench the hot reaction gases (about 1750°K). The quench feed becomes partly cracked, mainly to ethylene. Immediately below the anode pipe, A, the exiting hot reaction mixture is cooled to a temperature of about 450°K by means of a water spray, W. The electrodes, A and C, are water-jacketed. The cathode, C, is insulated from the other parts of the furnace which are grounded (insulator J). The start of the arc is accomplished by means of an ignition electrode, Z.

The arc is operated with 8000 kw direct current with a potential of 7000 volts and a current of 1150 amperes. The electrodes have a limited life. The cathodes last about 800 hours whereas the anodes have to be replaced after about 150 hours of operation. Disturbances of the arc, which were previously experienced due to deposits of hard graphite on the electrodes, have been successfully overcome.

The feed to the arc consists of a mixture of fresh hydrocarbons and recycle gas, and it is carefully adjusted to give optimum yields of acetylene and ethylene. The fresh hydrocarbon feedstocks are obtained from various sources and include refinery gases, liquefied C_3 and C_4 hydrocarbons, low-boiling gasoline fractions, and natural gas. The recycle gas contains the unreacted hydrocarbons and the cracked products other than acetylene and ethylene from the feedstock and the quench gas. Higher acetylenes, which amount to about 10 volume percent based on the amount of acetylene produced, are recycled to the arc.

Table 4 indicates the composition of a typical feedstock as well as the composition of the gas leaving the arc furnace.

Table 4. Composition of Feedstock and Reaction Product, Arc Process

Component	Volume percent	
	Feed gas, including recycle	Cracked gas ^a
C_2H_2	1.2	15.9
C_3H_4	1.0	1.0
C_4H_2	0.8	0.5
C_4H_4	0.7	0.5
C_2H_4	1.7	7.1
C_3H_6	2.3	0.9
C_4H_8	1.0	0.4
C_4H_6	0.4	0.3
CH_4	53.4	17.0
C_2H_6	10.2	1.2
C_3H_8	7.9	0.8
C_4H_{10}	12.5	2.1
C_5H_6	0.2	0.2
C_6H_6	0.4	0.4
C_7H_8		0.1
H_2	2.8	50.1
CO	0.8	0.7
N_2	2.7	0.8

^a The cracked gas contains the products produced in the arc from the feedstock as well as the products obtained from the quench hydrocarbons. The liquid quench feed amounts to 120 kg/1000 kw-hr and is composed of 25 kg C_3H_8 , 60 kg $n-C_4H_{10}$, and 35 kg iso- C_4H_{10} .

Taking into account the purification losses, the following operating requirements are necessary in order to obtain 100 kg of purified acetylene: 290 kg hydrocarbons (feedstock plus quench), 1030 kw-hr electric energy for the arc, 250 kw-hr electric energy for the separation unit, 150 kg steam.

The by-products amount to: 49.5 kg ethylene, 29 kg carbon black, 15 kg residual oil, 280 m³ hydrogen.

The quenched reaction gas passes through a multistep purification system which is discussed later under the heading, Separation and Purification of Hydrocarbon-Derived Acetylene.

The carbon black produced in the arc process is used in the rubber industry and in the manufacture of printer's ink.

Improvements made in recent years in the control power supply and arc design have substantially increased the efficiency and dependability of the Huels process. Because of the high requirements of electrical energy for the arc process, its economic situation is directly related to the availability and cost of electrical power.

Other processes using electrical discharges as the source of the required energy are the Ediger, and Schoch processes, which have been demonstrated in pilot-plant operation, and the processes described by Kroepelin and Schallus et al. (13-15). Up to this time, none of these techniques has attained commercial utilization. In addition to the Ediger process, patents of General Electric and others describe processes to crack liquid hydrocarbons by means of a submerged electric arc with the feedstock acting as its own quenching medium.

The Ediger process uses alternating current discharges submerged in a liquid hydrocarbon feedstock, such as crude petroleum, and tar, etc (14). It has been stated that the process produces a gas containing 30-35% acetylene. The workup of the process gas is similar to the purification technique developed for the Huels arc process (16). The development in Czechoslovakia of one-stage and two-stage ac arc processes has recently been reported by Cagas et al. who claim improved economics compared to dc arc and conventional processes (17). As in the case of the Huels process, the hot gas from the arc is prequenched with saturated hydrocarbons, which are partly cracked, mainly to ethylene.

The Schoch electric discharge process (15), developed at the University of Texas, employs a constant current alternating power supply to an electric discharge which operates in a suitable hydrocarbon vapor. The electric discharge occurs between a stationary electrode and a rotating blower wheel which forms the second electrode and which blows the gas feed through a V-shaped electric discharge space formed by the two electrodes. The colder gas surrounding the electric discharge area provides quick cooling for the reacted gas. The energy requirements depend, as usual, on the type of feedstock. Approximate requirements are listed in Table 5.

Table 5. Energy Requirements for the Schoch Electric Discharge Process

Feed	Kw-hr required per pound of acetylene	Percent of acetylene in cracked gas
methane	5-5.8	10-14
ethane	3.6-4	10-14
higher hydrocarbons, including vaporizable liquids	3.4-3.6	25-30

REGENERATIVE FURNACE PROCESSES

The regenerative furnace processes supply the necessary energy for the cracking reaction by heat exchange with a solid refractory material. An alternating cycle operation is employed whereby the hydrocarbon feed is heated by the hot refractory mass for a period of time to produce acetylene. Following this period, during which carbon and tars are deposited on the refractories, the process employs a combustion step in which the refractory mass is heated in an oxidizing atmosphere and the carbon and tar deposits are removed by burning. The refractories must resist both reducing and oxidizing atmospheres at temperatures around 1200°C . The refractories must also withstand the frequent and rapid heating and cooling cycles and, in the case of moving refractory beds (pebbles), abrasion.

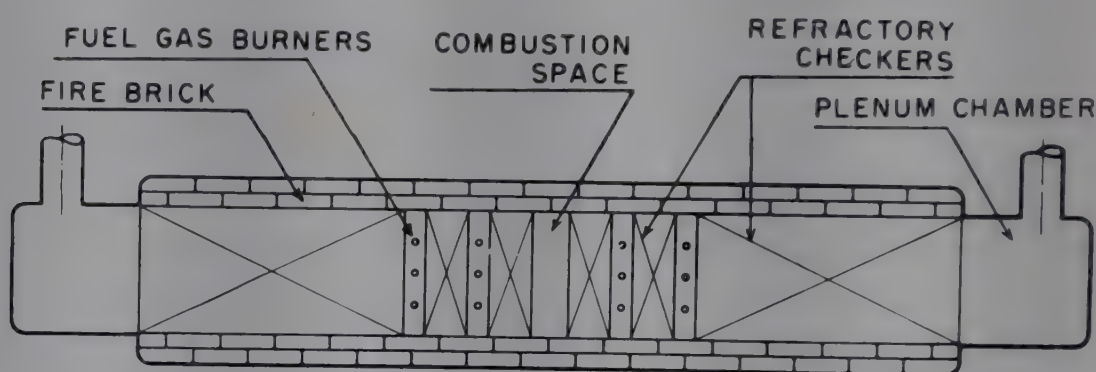


Fig. 4. Wulff furnace design.

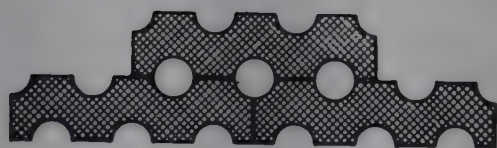


Fig. 5. Checker detail of Wulff furnace refractory.

After the acetylene is formed, the hot gases are quenched rapidly in order to preserve the acetylene formed in the reaction. As in other hydrocarbon-to-acetylene processes, this is accomplished with water sprays, or by passing the cracked gas through a second regenerative furnace section in which the gas is cooled while warming the furnace.

The regenerative technique is best exemplified by the Wulff process which has been in operation at Los Angeles, California since 1952, and which produces over one million pounds per year of bottled welding-grade acetylene. This process can use any gaseous or vaporizable hydrocarbons as feedstock. Hydrocarbons above methane are preferred because of higher conversion per pass.

The Wulff regenerative furnace consists basically of two masses of high-purity alumina refractory tile having cylindrical channels for gas flow and separated by a central combustion space as shown in Figure 4 and Figure 5. Its cyclic operation has four distinct steps, each of approximately one minute in duration, the sequence being pyrolysis and heat in one direction followed by pyrolysis and heat in the other direction. Continuity of cracked gas output is achieved by installing Wulff furnaces in pairs.

The regenerative nature of the Wulff operation permits the recovery of most of the sensible heat in the cracked gas. The gases leave the furnace at temperatures below 800°F , thus obviating the need for special high-temperature alloys in the switch valve and piping system.

The maintenance of low hydrocarbon partial pressures by the use of dilution steam and/or vacuum permits the achievement of the necessary short pyrolysis residence time (of the order of several hundredths of a second) favoring high acetylene yields. As practiced at the Wulff plant, the low hydrocarbon partial-pressure requirements necessitate vacuum pumps for both cracked gas and combustion gas. The furnaces are operated at a pressure of about 0.5 atmosphere absolute.

Since the combustion gas and the cracked gas do not mix, there is no dilution of the cracked gas by combustion products. Any fuel gas will serve for furnace heating, including the plant off-gas.

A Wulff plant is very flexible because the demonstrated ratio of acetylene to ethylene can be varied at will from nearly 4:1 to 1:4 or lower, depending on the feed-stock. Since the Wulff plant is also able to crack any vaporizable hydrocarbon, it can be seen that this plant is remarkably versatile.

When cracking propane for acetylene as the main product with ethylene being desired, the acetylene concentration in the cracked gases will range from 14 to greater than 16 mole percent and the ethylene concentration will range from 8 to 13 mole percent.

A typical cracked gas analysis under these conditions is listed in Table 6 for propane feed (18).

Table 6. Propane-Feed Cracked Gas Analysis

Component	Mol percent
acetylene	14.4
hydrogen	48.6
methane	17.5
ethylene	8.3
methylacetylene	0.4
vinylacetylene	trace
diacetylene	0.2
carbon monoxide	6.6
carbon dioxide	1.2
nitrogen	1.7
heavy hydrocarbons	1.1

Typical yields for acetylene plus ethylene (once-through cracking) on propane feed range from 51 to 59%, by weight on feed, for acetylene to ethylene ratios of 3.5:1 and 1:3.5, respectively.

The Wulff plant gas purification method employs a single-solvent absorption system using dimethylformamide (DMF) as the solvent (19). The cracked gas is compressed and first contacted with a small DMF wash to remove water, diacetylene, and higher boiling components. The next step is the absorption of acetylene in DMF. Off-gas from this operation is water-scrubbed and used as plant fuel gas.

The rich solvent stream from the acetylene absorber is selectively stripped to remove components less soluble than acetylene, and the acetylene is recovered in a product column. Higher acetylenes stripped from the solvent are cycled to the furnaces.

It has been reported that relatively minor modifications to the existing Wulff plant purification system make it capable of producing high-purity acetylene as contrasted with its normal (98% +) welding-grade acetylene product specification.

Modifications of the regenerative furnace technique which eliminate the necessity of vacuum pumps for both cracked gas and combustion gas by operating under atmospheric pressure have been revealed by Oldershaw and Levine in the U.S. and Kunugi et al. in Japan (20,21). Oldershaw et al. work with undiluted methane and obtain an acetylene concentration of over 11% by volume in the cracked gas. Kunugi uses hydrogen as diluent and operates the pyrolysis at higher temperatures, ie, in the case of methane at 1400°C instead of 1100°C as employed by Wulff. At the optimum dilution ratio of methane-to-hydrogen of 1:3.7, the cracked gas contains about 6.5% by volume of acetylene. It has been reported that the process which was developed at the University of Tokyo is being modified for the use of coke oven gas as hydrocarbon feedstock.

COMBUSTION PROCESSES

In the combustion or flame processes the necessary energy is imparted to the feedstock by the partial combustion of the hydrocarbon feed (one-stage process), or by the combustion of residual gas or any other suitable fuel and subsequent injection of the cracking stock into the hot combustion gases (two-stage process).

One-Stage Combustion Processes. A detailed discussion of the kinetics for the pyrolysis of methane for the production of acetylene by partial oxidation and some conclusions as to reaction mechanism have been given by Leroux and Mathieu (22).

There are several commercial versions of this technique, including the widely used BASF process (formerly called Sachsse process) and its various modifications with an all-over similar design (23). Natural gas or other methane-rich feedstock is mixed with a limited amount of oxygen insufficient for complete combustion, and fed through a specially designed distributor or burner to a single reaction zone in which ignition occurs. Improved results are claimed for variations of the original BASF partial-oxidation process which involve, for example, the preheating of the separate gas streams and an improved burner device, the SBA (Société Belge de l'Azote) process. (24); or preheating the premixed composite feed (Hydrocarbon Research, Inc., Delhi-Taylor Oil Corp.) (25,26). The Montecatini process, in addition to the separate preheating of the hydrocarbon feed and of the oxygen, employs pressure operations of up to six atmospheres absolute (27). In contrast, the process described by Tsutsumi of the University of Osaka, Japan, operated at reduced pressure of 200–300 mm Hg at temperatures of 1200–1500°C (28–30). The Montecatini process, like the Huels arc process, effects partial cooling of the burner gas by injecting higher hydrocarbons after the flame, resulting in the production of ethylene and some additional acetylene.

The preheating of the feed oxygen and methane, which is usually carried up to 500°C or above, supplies part of the energy requirement and thus, by making it possible to use less oxygen, reduces the dilution of the acetylene produced by carbon oxides and hydrogen.

The design of the burner is of considerable importance and has been given particular attention. The combustion of the gas mixture must be as uniform as possible across the reaction chamber so that the residence time of the reactant hydrocarbon is as short and as uniform as possible. Preignition, stability and blow-off of the flame, the possibility of backfiring through the ports of the burner head, and the deposition of carbon on the burner walls depend on the burner design and the velocities of the gas

and the flame. The proven technical feasibility of the partial combustion processes is caused by the high rates of the combustion reaction and of the formation of acetylene, together with the relatively slow rate of decomposition of acetylene and feed hydrocarbon to carbon and hydrogen.

The flame temperature reaches an average of 2700-2800°F. The residence time for the reaction is only 0.001-0.01 seconds. The pyrolysis products are rapidly quenched by means of one or more water sprays located in the lower part of the reactor. The effluent gases pass through scrubbers for the removal of most of the water and soot.

The yields of acetylene based on carbon in the natural gas feed vary somewhat for the various processes from 30-36% by weight. The composition of the cracked gas from a typical one-stage combustion process (BASF) is given in Table 7 for a natural gas feedstock.

Table 7. Composition of BASF Process Gas

Component	Percent by volume
acetylene	8.5
hydrogen	57.0
carbon monoxide	25.3
carbon dioxide	3.0
methane	4.0
higher acetylenes	1.0
inert material	1.0

So-called tonnage oxygen with a purity of 95-98% is normally used as the oxidant. Although more expensive than air, its use gives several economic advantages, such as a higher acetylene concentration in the cracked gas which results in lower purification costs. In addition, the plant off-gas obtained after separation of the acetylene contains high contents of hydrogen and carbon monoxide which, after further treatment, can be used for the synthesis of methanol or ammonia. The utilization of the off-gas is of considerable importance in establishing satisfactory economics for the partial combustion processes.

Figure 6 shows the design principle of the BASF converter. Methane and oxygen are separately preheated to about 1200°F and then mixed in a venturi-type mixing chamber in a molar ratio of about 0.6:1.0, oxygen to methane. The mixed gas is passed to the flame space through a plurality of tubular channels in a burner block. The gas velocity in the burner block channels must be maintained higher than the flame propagation velocity, and the gas velocity in the flame chamber should be maintained low enough to avoid blow-out of the flame. About one third of the methane entering the burner is cracked to acetylene, the remainder is burned. The cracked gas is immediately quenched by water sprays, scrubbed for the removal of water and soot, and compressed for further purification.

The overall yield of acetylene is 30% based on methane, and the oxygen requirement is about 4.75 pounds per pound of acetylene produced. Individual BASF converters have a capacity of up to 20 tons of contained acetylene per day. The SBA one-stage converter, which is entirely metallic, is reported to produce 20-25 tons of acetylene per day when it is operating on methane feed with an oxygen consumption of 4.6 pounds per pound of acetylene produced.

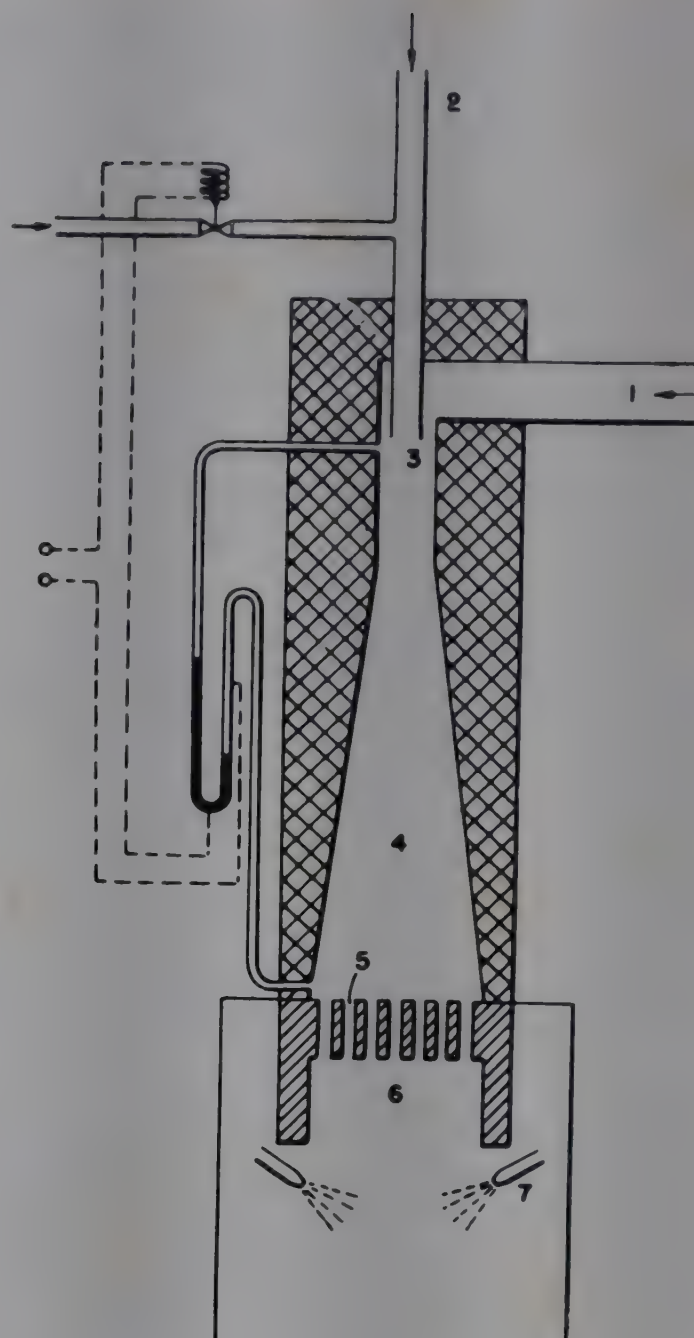


Fig. 6. BASF acetylene converter. 1. Methane feed. 2. Oxygen feed. 3. Zone of initial mixing of methane and oxygen. 4. Completion of mixing. 5. Hole in burner block. 6. Flame space. 7. Water quench.

The BASF partial combustion process and variations thereof are in commercial use in a considerable number of large plants. Table 8 gives a partial listing of various process installations.

Table 8 is by no means a complete listing of the commercial installations producing acetylene by the partial combustion process. The Montecatini process, for example, is in use in three nonlisted plants located in Japan, and in other plants located in Poland and the U.S.S.R. (Urals). The total installed acetylene capacity by the Montecatini process is said to be about 330 million pounds acetylene per year (1961). SBA one-stage process installations are under construction in the U.S.A., U.S.S.R., and Rumania.

Two-Stage Combustion Processes. Instead of burning part of the feedstock itself, the two-stage combustion processes burn, in a first stage, process off-gases or any fuel gas of lower value than the hydrocarbon feedstock. The gaseous oxidant is used in nearly stoichiometric ratio to the fuel in order to provide the necessary

Table 8. Principal Commercial Installations Which Use the Partial Combustion Process

Company	Location	Converter used	Capacity, ^a million pounds
Union Carbide Chemicals	Texas City, Texas	Union Carbide	75
Azienda Nazionale Idrogenazione Combustibili	Ravenna, Italy	Union Carbide	more than 75
Societa Italiana Seria Acetica Sintetica	Milan, Italy	BASF	80
SIC Edison	Venice, Italy	BASF	86
Monsanto Chemical	Texas City, Texas	BASF	80
American Cyanamid	Luling, Louisiana	BASF	100
Monochem	Geismar, Louisiana	BASF	80 ^b
Aquitaine Chimie	Pan, France	BASF	60
Kyowa	Niigata, Japan	BASF	20 ^b
Rohm & Haas	La Porte, Texas	BASF	40
Dow Chemical	Freeport, Texas	Dow	40-50
Montecatini	Novarra, Italy	Montecatini	15
Diamond Alkali	Deer Park, Texas	Montecatini	40
Dusikarnj Cechj	Most, Czechoslovakia	Montecatini	35
Lonza Usines Electroch.	Switzerland	Montecatini	35
Houilleres du Bassin de Lorraine	Carling, France	SBA	12
Tennessee Gas Transmission	Houston Ship Channel, Texas	SBA	100

^a Estimated 1961. ^b Due on stream in late 1962.

high-temperature heat for the cracking reaction. As the hot gases leave the flame zone at about 2000°C and enter the second-stage reaction chamber, the hydrocarbon feedstock is injected into the combustion gases for cracking. The mixture of cracked gas and combustion products is rapidly quenched, usually by means of water, to fix the acetylene so produced.

Air or oxygen can be used in the combustion step. Since with oxygen as the oxidant the temperature in the flame zone may be too high, low-pressure steam may be added to lower the temperature of the combustion gases prior to the injection of the feedstock. The total mass of hot gas available for mixing with the hydrocarbon feedstock is thereby increased.

The two-stage flame cracking processes use light hydrocarbon feedstocks, such as liquefied petroleum gases or natural gasoline, and produce acetylene and ethylene simultaneously.

Several two-stage converters and processes have been described in the literature, including the Tennessee Eastman process (31), the Phillips Petroleum Co.'s pebble-heater process (32), and the processes developed by Farbwerke Hoechst A.G. in Germany (33), by Tsutsumi in Japan, and by SBA in Belgium (34).

The SBA two-stage process is used by Sumitomo Chemical Co. at Niihama, Japan, to manufacture 150 thousand pounds per day of concentrated acetylene and ethylene from naphtha.

The converter, as shown in Figure 7, consists of two superimposed chambers. In the first, or combustion, chamber the combustion in oxygen of a hydrogen-rich gas is effected in the presence of superheated steam. By means of a special design, the combustion takes place with the formation of a ring of short flames, surrounded by

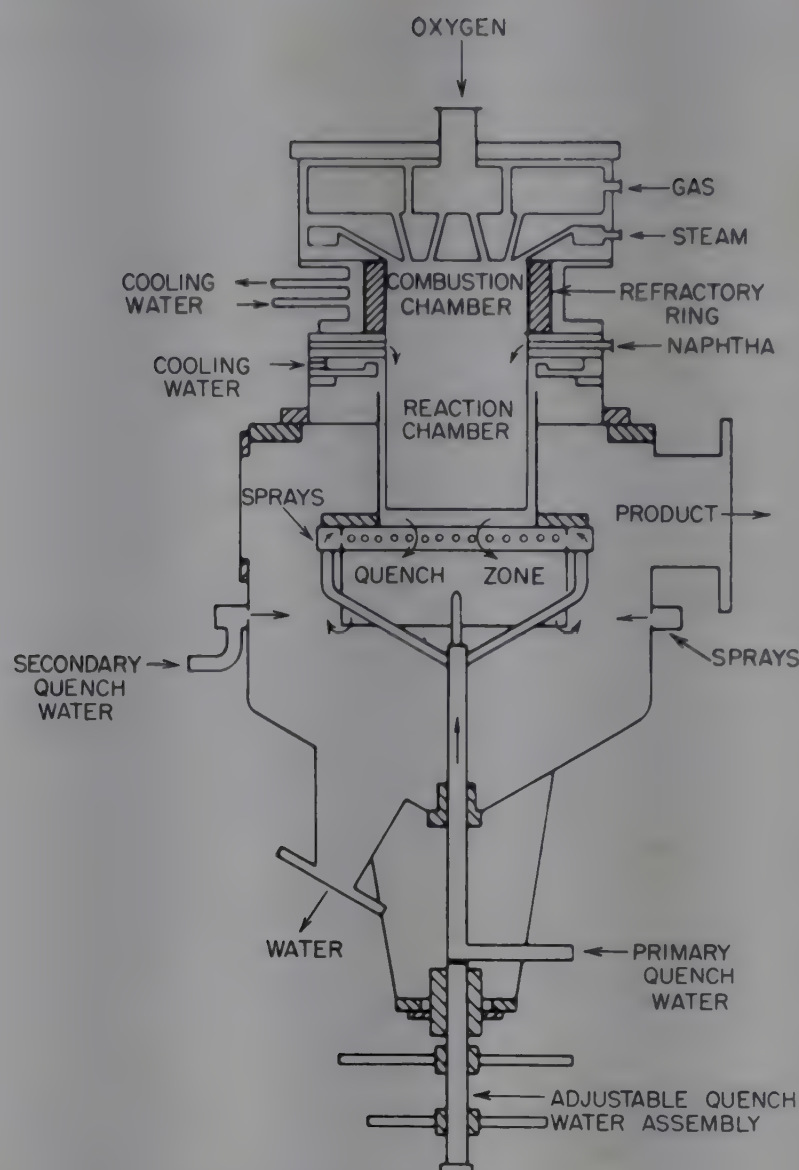


Fig. 7. SBA two-stage converter.

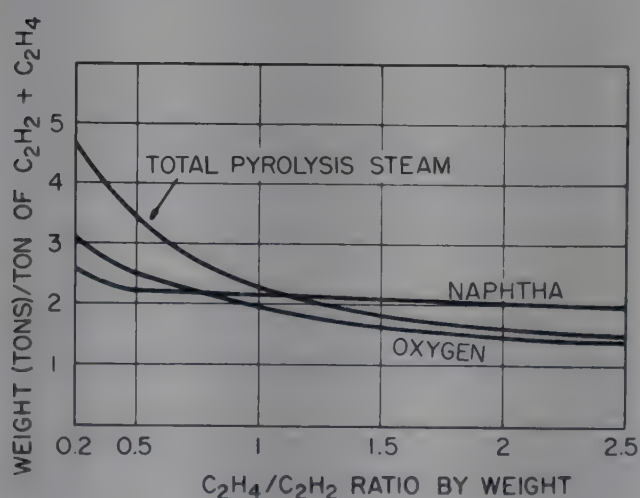


Fig. 8. Specific consumption per ton of concentrated acetylene and ethylene as a function of the ethylene/acetylene production ratio.

steam. The energy required for pyrolysis is highly concentrated and thermal losses are reduced to a minimum (34). In the second chamber, or pyrolysis chamber, the hydrocarbon feedstock is injected into the hot combustion gases. The reaction products are then thoroughly quenched so as to avoid all parasitic reactions.

With this type of burner a wide variety of raw materials can be used, ranging from propane to naphtha and also heavier hydrocarbons containing 10–15 carbon

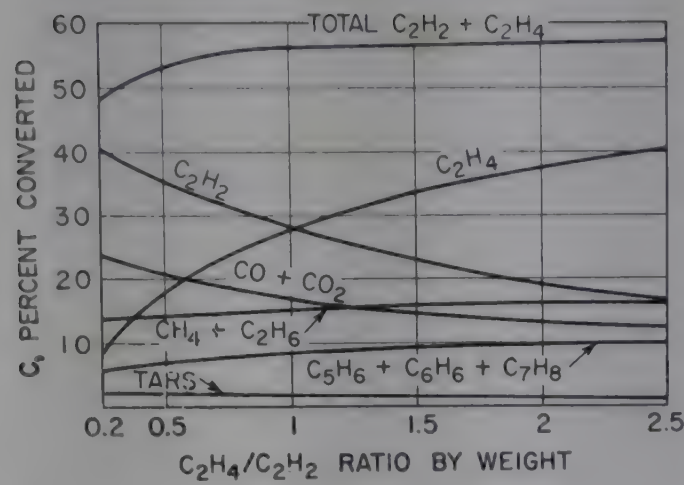


Fig. 9. Conversion rates of the naphtha into its derivatives as a function of the ethylene/acetylene production rate.

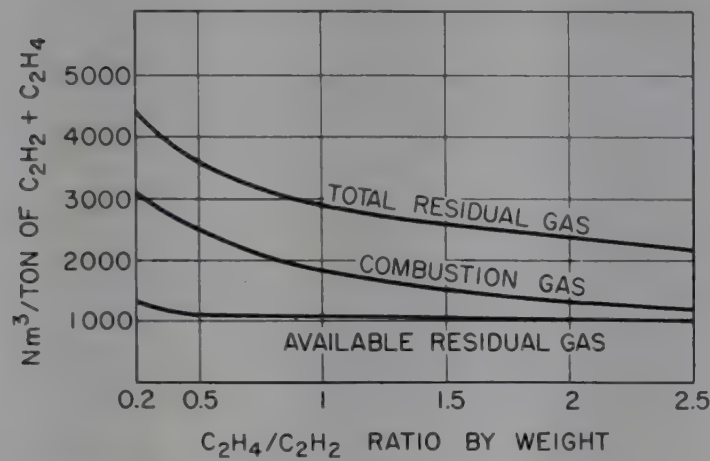


Fig. 10. Production of residual gas per ton of concentrated acetylene and ethylene as a function of the ethylene/acetylene production ratio.

atoms. In addition, the peculiar characteristics of the different raw materials which can be used enable, if necessary, the simultaneous production of acetylene and ethylene (and heavier olefins) in proportions which can be varied within wide limits without requiring basic modifications of the burner.

The ethylene/acetylene ratio may be fixed between 0.1 and 3, and the total yields of concentrated acetylene plus ethylene vary from 48–50% according to the value of this ratio. Figure 8 indicates the specific consumption of light naphtha, pyrolysis steam, and oxygen in tons per ton of ethylene/acetylene ratios of 0.2 to 2.5, whereas Figure 9 shows the conversion rates to products and by-products as a function of the same ratio. Figure 10 indicates the production and consumption of residual gas in cubic meters per ton of acetylene/ethylene concentrate for various product ratios.

The two-stage HTP (high-temperature pyrolysis) process is being operated by Farbwerke Hoechst in Germany. The Hoechst plant is designed to manufacture 100 million pounds per year of acetylene and ethylene from hydrocarbons. The process is illustrated in Figure 11.

The cracking stock for the HTP process can be any suitable hydrocarbon. With hydrocarbons above methane, the ratio of acetylene to ethylene can be varied over a range of 70:30 to 30:70. Total acetylene plus ethylene yields, as weight percent of the feed, are noted in Table 9.

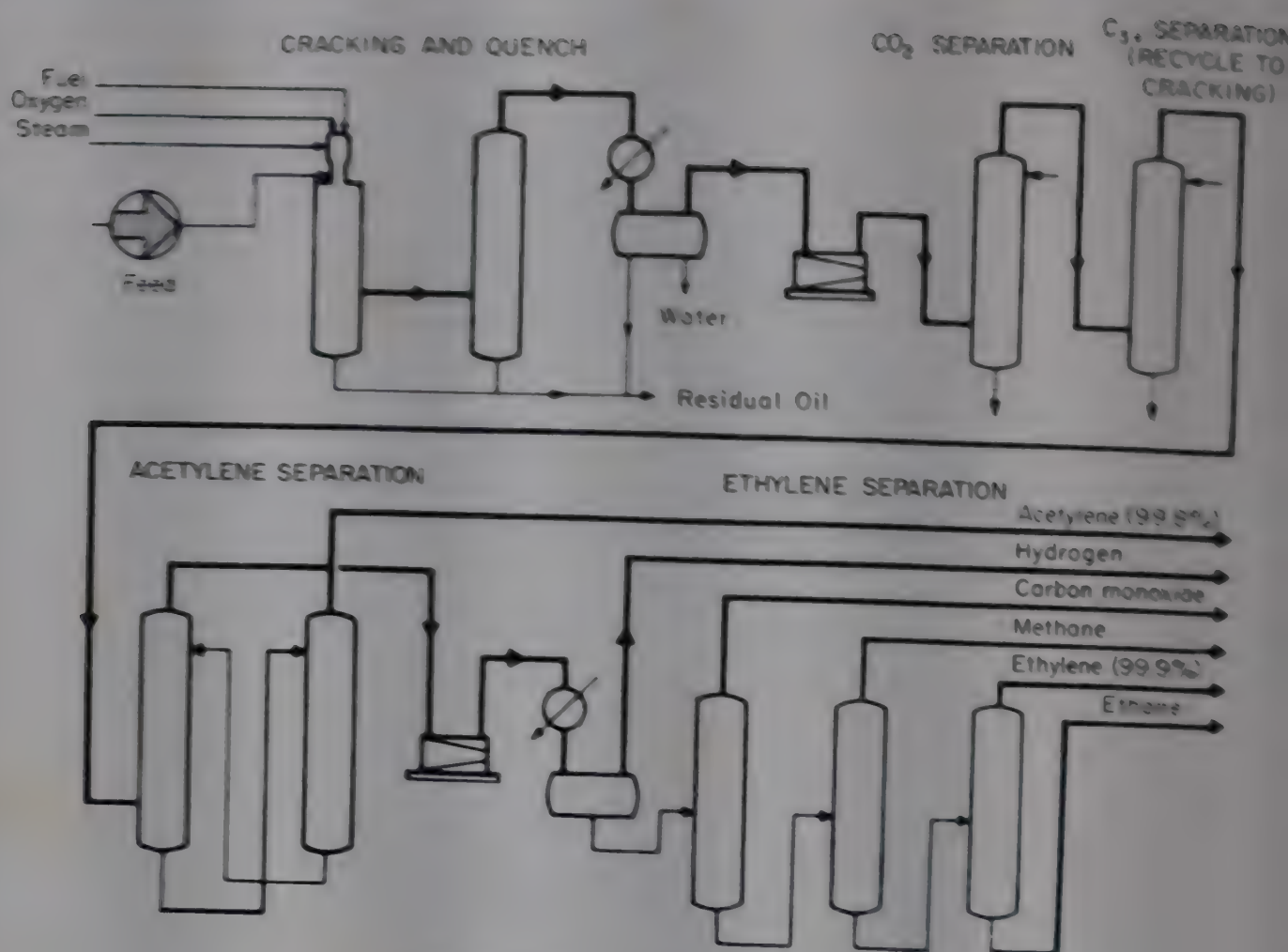


Fig. 11. Hoechst HTP process.

The Hoechst burner is a water-cooled unit of all-metal construction. Fuel gas, which may be hydrogen, hydrocarbons, or off-gas from the process, is burned with oxygen in near stoichiometric amount in the combustion chamber. The hot combustion gases (tempered with dilution steam), together with the hydrocarbon feedstock injected, preferably as a vapor, enter the reaction zone where cracking of the feedstock takes place to form acetylene and ethylene. Residence time in the reaction zone is very short—of the order of 0.001 second. A rapid quench in specially designed

Table 9. High-Temperature Pyrolysis Process Yields

Feed	Yield, wt %	Product
methane ^a	40.0	acetylene
butane	54.8	acetylene + ethylene (50:50)
light naphtha	54.0	acetylene + ethylene (30:70)
	50.0	acetylene + ethylene (70:30)

^a Methane recycled.

equipment is effected to reduce the gas temperature below cracking temperatures. Available heat is recovered in this operation by generating steam for use elsewhere in the process. Heavy hydrocarbons are separated from the gas and may be used as fuel. The cooled cracked gas is compressed prior to entering the purification train. Carbon dioxide is removed by the conventional absorption-desorption technique employing a solvent specifically developed by Hoechst for this purpose.

The process gas is then cooled and dried and the higher acetylenes are removed. C_2 and heavier hydrocarbons are separated and, with the higher acetylenes, are recycled to the reactor with the feedstock.

The remaining gas is treated with a selective refrigerated solvent to absorb acetylene which is then recovered as a 99.8% or greater purity product. The exit gas from the acetylene separation, chiefly a mixture of ethylene, ethane, hydrogen, carbon monoxide, methane, and inerts, is processed through conventional means, such as low-temperature fractional distillation, to recover high-purity ethylene (99.8%). Ethane recovered in this operation may be recycled to cracking or combined with the fuel gas stream. The residual gas from ethylene recovery, rich in hydrogen and also containing methane and carbon monoxide, may be recycled to the burner for use as fuel gas. Alternately, it can be used as a source of synthesis gas for the manufacture of ammonia and methanol.

OTHER PROCESSES

A novel and possibly significant approach to the conversion of hydrocarbons to acetylene has been described by Schallus and Goetz of Knapsack-Griesheim A.G., Germany (35).

Preheated hydrogen (1000°C) is led through an electric arc where it is further heated to such a temperature that it is partially or completely decomposed into its atoms. The hydrocarbon feed is then mixed with this plasma outside the arc whereby the recombination of the hydrogen atoms to molecular hydrogen provides the energy for the cracking of the hydrocarbon to acetylene. The reaction mixture is quenched in the usual manner with water to 100°C . It is claimed that in the case of propane feed 80% of the carbon content of the hydrocarbon is converted to acetylene, 7.3% to propylene, 9% to ethylene, and 3.6 % to methane. Higher acetylenes and soot were not formed.

Using the same experimental approach, Schallus et al. report that they were successful in producing acetylene from completely degassed powdered lignite (35).

Leutner and Stokes of Temple University, Philadelphia, Pa., report (May 1961) that by using a low-voltage argon plasma jet they were able to convert methane to acetylene with yields of 80% and above by weight, based on the carbon in the hydrocarbon feed (36). A more detailed description of the plasma jet technique for the preparation of gaseous endothermic compounds, such as acetylene, is given by Grosse et al. (37).

In addition to the new approaches mentioned it has been suggested that the use of shock-tube techniques, which provide temperatures as high as the arc and plasma processes, may find commercial application for this type of processing (38).

SEPARATION AND PURIFICATION OF HYDROCARBON-DERIVED ACETYLENE

The pyrolysis of methane results in a cracked gas which is relatively low in acetylene content and which contains predominantly a mixture of hydrogen, nitrogen, carbon monoxide, carbon dioxide, unreacted hydrocarbons, acetylene, and higher homologs of acetylene. In cases where a higher hydrocarbon than methane is used as feedstock, the converter effluent contains, in addition to these pyrolysis products, olefins, such as ethylene, propylene, propadiene, and butadiene, and aromatics, such as benzene, naphthalene, and miscellaneous higher hydrocarbons. Most acetylene proc-

esses produce significant amounts of carbon black and tars which have to be removed before the separation of acetylene from the gas mixture can begin.

The isolation of the acetylene contained in the effluent of the various converters presents a complicated problem. The unstable, explosive nature of acetylene imposes certain restrictions and limitations on the use of the customary separation techniques developed with great efficiency for other hydrocarbon systems. The results of decomposition and detonation studies on acetylene and its mixtures with other gases indicate that operating conditions where the partial pressure of acetylene exceeds 15 to 30 psia should be avoided. Similar limitations apply to the operating temperatures which should not exceed 200–220°F. Low temperatures may lead to the appearance of liquid or solid acetylene or its homologs with concomitant danger of unexpected and sudden decompositions. In view of these severe operating restrictions it is not surprising that all commercial processes for the recovery of hydrocarbon-derived acetylene are based on absorption/desorption techniques using one or more selective solvents.

Of the many solvents proposed, only a few have found commercial application, including water (Huels), anhydrous ammonia (SBA), chilled methanol (Montecatini), *N*-methylpyrrolidone (BASF), butyrolactone, acetone, dimethylformamide, and hydrocarbon fractions.

The separation and purification of acetylene is further complicated by the presence in the pyrolysis gas of higher acetylenes which dissolve in the usual acetylene solvents and polymerize rather easily. The removal of these constituents is a necessity, particularly in view of the final utilization of the acetylene in chemical synthesis. This removal can be accomplished by scrubbing the dilute or concentrated acetylene with small amounts of a suitable mineral oil or other organic solvent (Schoch, SBA, Wulff) or by low-temperature fractionation (Huels). In the latter case, the concentrated, dry acetylene is cooled close to the freezing point (195°K) whereby the higher acetylenes are liquefied and removed as a solution in methanol or benzol.

The carbon black (soot) produced in the partial combustion and electrical discharge processes is of rather small particle size and contains substantial amounts of higher, mostly aromatic, hydrocarbons which may render it hydrophobic, sticky, and difficult to remove by filtration. Electrostatic units, combined with water scrubbers, moving coke beds, and bag filters, are being used for the removal of soot. After removal of carbon black and tars, the recovery of the acetylene from the pyrolysis gas mixture is accomplished in multistep separation systems as illustrated by the Huels separation and purification system described below.

Huels uses an elaborate purification and separation system (11) whereby the bulk of the carbon black (about 60%) is removed by means of cyclone separators as a dry product; subsequently, the hot gases are contacted in at least one scrubber with water which removes another 38–39% of the original soot content. The final carbon black removal occurs in a combined oil–water scrubbing system, resulting in an effluent gas containing only 3 mg/m³ of soot (39). Hydrocyanic acid is subsequently removed by a water wash. If sulfur-containing hydrocarbons are used as the feedstock, the hydrogen sulfide is removed by treatment with *luxmasse*, or hydrated iron oxides.

Water is then used for the recovery of the acetylene from the gas mixture. The purified gas is compressed to 19 atm abs in four-stage compressors with a capacity of 1300 m³ of free gas per hour each, and countercurrently washed with water in 30-m high towers, containing 65 plates each. The saturated solution of acetylene is withdrawn from the bottom of the wash towers while the other gases, consisting of hydro-

carbons and hydrogen, essentially free from acetylene (acetylene content less than 0.05 volume percent), are withdrawn from the top. The acetylene–water solution is pressure-released in four stages. The gas from the first pressure-release step is recycled to the compressors. The last two pressure-release steps operate under reduced pressures of 0.2 atm abs and 0.05 atm abs respectively. The gas released in the last three steps contains about 10% by volume of higher acetylenes which are separated out by low-temperature liquefaction and fractionation whereby the gas is cooled down almost to the freezing point of acetylene. The purified acetylene is obtained as a completely dry gas. Table 10 gives the composition of the purified acetylene.

Table 10. Composition of Purified Acetylene

Component	Volume percent
C ₂ H ₂	97
C ₂ H ₄	1.4
CH ₄	0.5
C ₃ H ₄ (methylacetylene)	0.4
H ₂	0.6

The nonabsorbed exit gas, which leaves the wash-towers under a pressure of 18 atm abs, is separated by refrigeration in a Linde plant into its components. Ethylene is concentrated in separate equipment. The remaining hydrocarbons are recycled to the arc furnace. By-product hydrogen, which is obtained under 17 atm abs pressure, is used for hydrogenation purposes; it contains 98 volume percent hydrogen and 2 volume percent nitrogen.

The separation processes are, in a number of cases, linked with the recovery of useful by-products of the pyrolysis, such as the segregation of carbon monoxide and hydrogen for use in the synthesis of methanol or ammonia. If hydrocarbons higher than methane are used as feedstock, the isolation and purification of the coproduct ethylene becomes of equal importance with that of acetylene. Pyrolysis by-products with three or more carbon atoms, such as methyl- and vinylacetylenes, diacetylene and the like, which are present only in small quantities, are generally collected as one fraction and disposed of by recycling to the cracking step.

The recovery and purification steps are expensive operations and require a capital investment which is usually substantially higher than that required for the converter. The choice of the most suitable solvent and the selection of an efficient separation process have considerable bearing on the economics of a given pyrolysis process.

The purity of pyrolytic acetylene depends solely upon the effectiveness of the engineering applied in the purification system. Most separation processes in commercial use are capable of producing acetylene of high purity approaching 100%.

Explosive Behavior

Acetylene is an unstable compound with a strong tendency to decompose into its constituent elements, carbon and hydrogen, with the evolution of a considerable amount of heat. Unlike any other industrial gas, acetylene can decompose either slowly or with explosive violence, even in the absence of oxygen, and detonates at pressures as low as 0 to 1 psig. The character, course, and ultimate force of an acetylene decomposition are dependent on a number of factors: the initial pressure

and temperature of the acetylene-containing system, its size and shape, the amount and nature of diluents, such as water vapor or other gases, the intensity of the initiation energy which triggered the decomposition, and the size of the initiation source. The handling of acetylene presents serious complications which are unique for a gas so widely used in industrial applications.

The practice, established during the last decade, of transporting large volumes of compressed acetylene through pipelines from a central producing station to industrial users, as well as the growing use of pressure acetylene in chemical manufacturing operations, has intensified the usual handling problems encountered with this gas. Detailed studies of the explosive behavior of acetylene under varying conditions of temperature and pressure have been published and the explosion limits of mixtures of acetylene with other gases have been determined (40-46).

An acetylene decomposition can proceed in several different ways, characterized primarily by the rate of propagation. Slowest of these decompositions is a stationary or slowly moving deflagration or flame, which may increase in speed to almost any velocity less than sonic, resulting in a fast decomposition, an *explosion*. When the decomposition flame travels into the unburned gas at a rate above the speed of sound, a *detonation* results.

It has been proved that once an acetylene decomposition has started (eg, due to a sufficiently high, local temperature increase of the gas, caused by a spark) propagation of the decomposition may or may not occur in the gas-containing system, depending on the factors mentioned above. Assuming a flame front has been established in a container such as a pipe, the rate of propagation will depend on the initial pressure and temperature in the line as well as on local conditions, such as the pipe diameter and the rate of flow. The heat loss on the wall of the pipe through which the flame proceeds reduces the temperature and the flame velocity. A decrease in flame velocity increases the heat loss through the wall so that under certain conditions a flame front in a pipe line may become stationary or even extinguished.

During a fast decomposition of acetylene, a flame front and a separate pressure or shock front are produced. These fronts transfer energy to adjacent acetylene molecules and cause them to decompose, thus supporting and spreading decomposition.

The influence of the gas flow through a system is of importance to the propagation of a decomposition, particularly in the case of turbulent flow. In turbulent deflagration, the surface of the flame front is increased due to pulsation. The flame velocity increases with increased turbulence, increased density, and increased temperature of the unburned portion of the gas. Therefore, if a flame does propagate through a pipe of sufficient length, the flame will accelerate due to the turbulence of the unburned gas. This acceleration of the flame front can lead to the development of a detonation wherein ignition of the unburned gas is caused by the high temperature developed by the compression of the gas in the shock wave. Under these conditions, flame front and shock front have fused together.

When the forward motion of the gas in a detonation wave is stopped by an obstruction, eg, a sharp turn or the closed end of a pipe, its pressure increases and a shock wave is reflected back to the ignition end. The reflected pressure is about 50 times the pressure of the gas into which the detonation wave moved before striking the obstruction.

A slow acetylene decomposition may travel at a speed of one or several inches per second whereas an explosion wave will propagate at an initial speed of 10-15 feet per

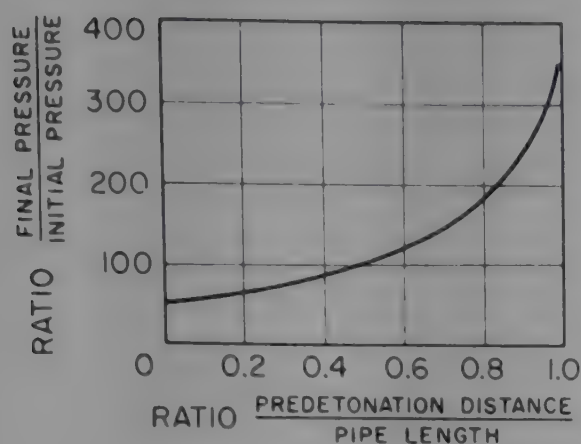


Fig. 12. Explosion pressure-ratios attainable by cascading explosion process in acetylene as a function of predetonation length/pipe length value (47). Calculated for 49 psig initial pressure; applies approximately to any initial pressure.

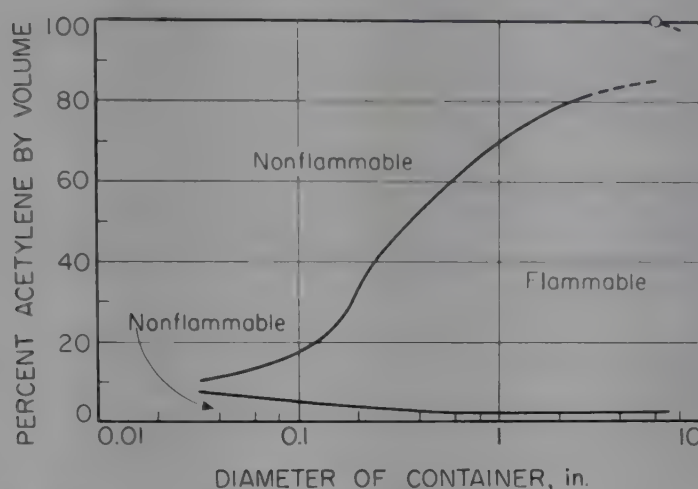


Fig. 13. Flammability limits of acetylene-air mixtures at atmospheric pressure in containers of various diameters. Direction of flame propagation was horizontal for tubes smaller than 0.4 in. ID and for 6 in. ID tube with 100% acetylene, otherwise upward. Ignition end of tube was open for tubes smaller than 0.4 in. ID, otherwise closed.

second. Detonation waves travel several times faster than sound and have been measured at about 6000 feet per second.

Experimental acetylene decompositions, carried out under controlled conditions, indicate that explosions give pressure rises up to about 10–12 times the initial pressure, and detonation pressures may reach about 50 times the initial pressure.

If a detonation forms only after a subsonic decomposition has traveled a large fraction of the length of a pipe and thus increased the density of the unburned gas, the maximum pressure may be much more than 50 times the initial pressure.

Figure 12 shows the magnitude of the pressure that can result from such a cascading process, plotted as a function of the ratio of the predetonation distance to the pipe length (47). There is experimental evidence that the cascading effect is not unusual when acetylene, in pipes of commercially used sizes, is ignited (48), and that the resulting pressure ratios are of the indicated magnitude.

The influence of the length of an acetylene-carrying pipe on the peak pressure obtained in a decomposition has been checked by a number of investigators. The data indicate that once a flame front has been established across the diameter of a tube and that tube diameter and system pressure are large enough to permit detonation, explosion and detonation must be expected to follow, provided the tube is sufficiently long. The minimum tube length necessary to let decomposition accelerate into an explosion or detonation depends primarily on the initial pressure and may vary from a few feet at pressures around 100 psia to several hundred feet at pressures of about 15 psia (47).

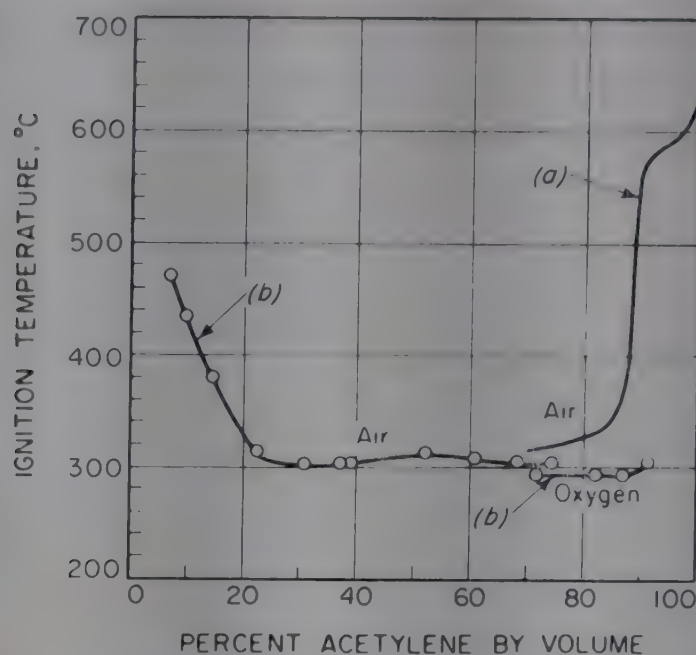


Fig. 14. Ignition temperature of acetylene-air and acetylene-oxygen mixtures. Gas initially at 1 atm absolute. Container (a) quartz tube 0.67 in. ID \times 36 in. length (41); (b) 131 cm³ bulbous enlargement in quartz tube (49).

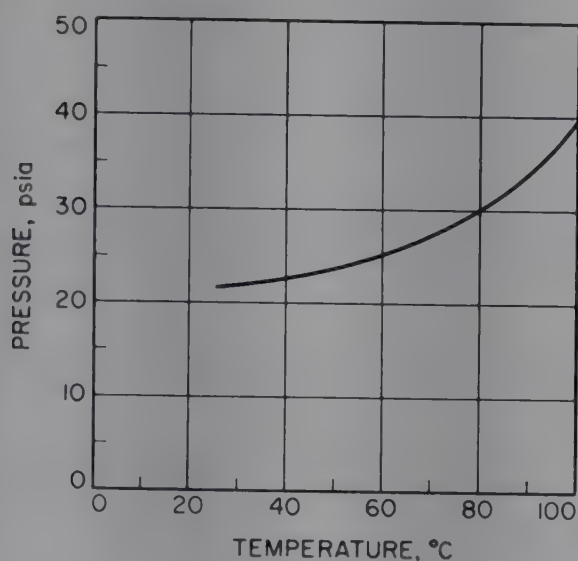


Fig. 15. Pressure required for ignition of acetylene saturated with water vapor at various temperatures. Initiation: fused platinum wire (40,50,51).

Flammability and Ignition Temperatures of Mixtures of Acetylene with Air and Oxygen. The experimentally determined flammability limits for acetylene-air or acetylene-oxygen mixtures vary somewhat with the physical dimensions of the test equipment used. The usually stated figures for mixtures with air are 2.5–2.8% and 80% acetylene by volume; with acetylene-oxygen mixtures the higher limit is 92–93% acetylene with the lower limit being about the same as with air. Increasing the temperature or the pressure of an acetylene-air mixture tends to widen the range of flammability. Figure 13 indicates the flammability limits of acetylene-air mixtures at atmospheric pressure in containers of various diameters.

Ignition temperatures for dry mixtures of acetylene with air or with oxygen, as determined in quartz tubes at atmospheric pressure, are shown in Figure 14. Increased pressures lower the ignition temperature (41).

Ignition of Mixtures of Acetylene with Nonreactive Gases. The presence of nonreactive diluent gases, such as nitrogen, carbon dioxide, propane, or vapors of water and acetone exerts a stabilizing influence on acetylene as shown in Figures 15, 16, and 17. The stabilizing effect of the nonreactive diluents varies with their con-

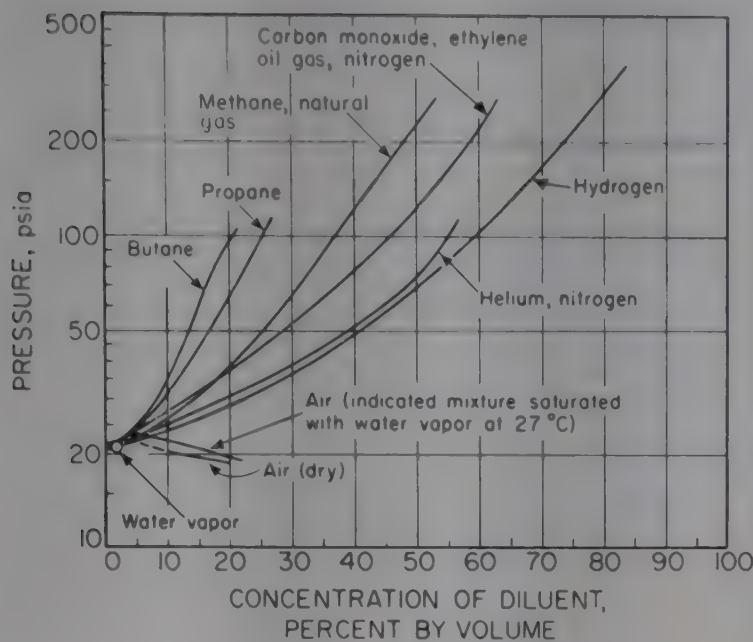


Fig. 16. Pressure required for ignition of mixtures of acetylene and a diluent gas at room temperature. Initiation: fused platinum wire. Container: 2 in. ID × 12 in. length; 10.6 in. ID × 10.6 in. length; 4 in. ID × 10 in. length (40,45,50,51).

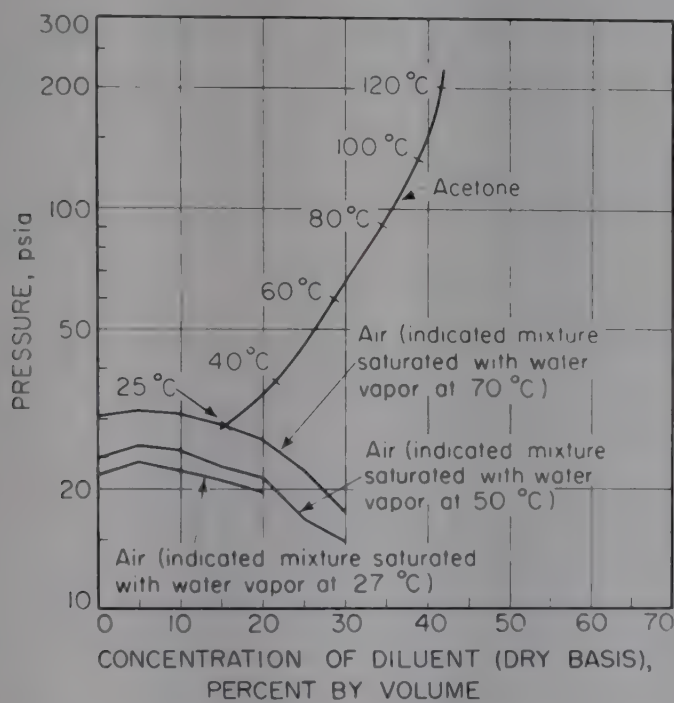


Fig. 17. Pressure required for ignition of acetylene–acetone and water-saturated acetylene–air mixtures at temperatures needed to keep diluents in vapor form. Initiation: fused platinum or nichrome wire. Container: 10 in. ID × 81 in. length; 2 in. ID × 12 in. length (50,51).

centrations in the mixture and is approximately in the order of their molar heat capacity. Small percentages of diluent gas are not very effective.

Mixtures of acetylene with nonreactive gaseous diluents have found considerable interest and importance in connection with the use of acetylene under pressure in large-scale manufacturing operations, such as vinylations. Reppe of I. G. Farbenindustrie, Germany, developed suitable operating methods for the safe handling of dilute acetylene under pressures of up to several hundred pounds per square inch (46).

Explosive Behavior of Acetylene–Air and Acetylene–Oxygen Mixtures. Factors such as pressure, temperature, and the physical dimensions of the containing vessel will cause the normal burning of mixtures of acetylene with air or oxygen to proceed

either as a deflagration or as a detonation, ie, the burning proceeds at subsonic or at supersonic speeds. The presence of oxygen strongly enhances the probability of a detonation. A detonation has the ability to propagate through narrow passages which would stop straight acetylene decomposition (52). Predetonation distances are shorter with acetylene-containing oxygen than with acetylene alone, and the initial pressures required for a detonation to develop are lower. Acetylene-air mixtures develop at about the same deflagration and detonation pressures as straight acetylene. Acetylene-oxygen mixtures usually detonate rather than deflagrate, and the pressure is usually about 110 times the initial pressure (53-56).

The velocities of detonations of acetylene-air and acetylene-oxygen mixtures have been measured to be 2000 m/sec (15% acetylene, 85% air) and about 2940 m/sec (50% acetylene, 50% oxygen), respectively, (57-59). The cascading mechanism, common in straight acetylene decompositions, has also been observed with acetylene-air mixtures but not with acetylene-oxygen mixtures (56).

Handling of Acetylene

The design of equipment for the handling and use of acetylene must take into consideration the possibility of spontaneous acetylene decompositions, which, depending on various factors, such as pressure, temperature, and source of ignition, may proceed with explosive violence and lead to detonations. Decomposition in small vessels and short piping systems used at moderate pressures of 15 psig will result in maximum pressures not higher than about 12 times the initial pressure. However, in pipe lines of considerable length and of diameter sufficient to permit a detonation to develop, maximum detonation pressures of about 50 to several hundred times the initial pressure must be expected.

The establishment of exact design criteria and recommendations for the engineering of equipment for handling acetylene is not feasible due to the very pronounced influence of a great number of factors upon the initiation and course of acetylene decompositions. However, general recommendations have been made concerning the type of equipment for handling acetylene, including the use of suitable compressors, the construction of piping systems and of protective devices such as flame and detonation arresters, and the use of proper materials of construction (60-62). The handling of acetylene under pressure requires special precautions which have been described in the literature (46,63).

Acetylene in Cylinders. Acetylene cylinders are constructed in such a way that they safely avoid the hazards of high-pressure acetylene. Cylinders built for other gases do not have these safety features and it is obvious that other cylinders must not be charged with acetylene. Likewise no attempt should be made to charge any other gas into an acetylene cylinder. One basic feature of safe construction lies in packing a porous mass with extremely minute cellular spaces into the acetylene cylinder so that no pockets of appreciable size remain where "free" acetylene in gaseous form can collect. A second safety factor is the use of acetone as a solvent. Acetone dissolves many times its own volume of acetylene; the solubility increases with rising pressure and with diminishing temperature. Since acetylene in a cylinder is not a free gas, but is held in solution in the acetone, a gage attached to the cylinder indicates what is known as the "solution pressure" in the cylinder. This pressure is greatly affected by changes in cylinder temperature, such as are experienced in winter and summer. For example, the gage pressure of a cylinder may be 230 psig when the

temperature is 70°F; if this same cylinder is allowed to cool to 0°F, the pressure will drop to less than 100 psig without any acetylene having been withdrawn. It is therefore obvious that the contents of an acetylene cylinder, unlike oxygen or nitrogen cylinders, cannot be determined accurately by pressure gage readings. Acetylene cylinder contents can, however, be accurately measured by weight, and it is on this basis that cylinder-charging operations are conducted. Weight of acetylene can be converted into standard cubic feet (atmospheric pressure and 60°F) by the factor of 14.5 cu ft/lb.

Acetylene cylinders are fitted with safety devices to release the acetylene in the event of an abnormally high temperature, as in a fire. In cylinders manufactured in the U.S., these safety devices contain a fusible metal that melts at about the temperature of boiling water. In large cylinders the devices take the form of replaceable plugs with a core of the fusible metal. Small cylinders may have such plugs or fusible metal passages in a valve or other cylinder accessory.

The most usual sizes of acetylene cylinders are those with nominal capacities of 10, 40, 100, 225, and 300 cu ft. So-called "*lighthouse*" cylinders used for marine navigation have capacities of about 1000 cu ft of acetylene.

The construction and shipping of acetylene cylinders in the U.S. follow the specifications and regulations of the Interstate Commerce Commission, which in turn follows the recommendations of the Bureau of Explosives of the Association of American Railroads. Specification ICC-8 applies to acetylene cylinders, and, among other things, requires them to meet certain chemical and physical specifications, to pass hydrostatic pressure tests, to possess fillers of 83% or more porosity, and to be protected by adequate safety-release devices. Each cylinder is required to carry the marking, ICC-8, plus a serial number, a tare weight, and a symbol. The cylinder must be registered with the Bureau of Explosives, together with reports of its manufacture and test. In addition, the date of manufacture and any subsequent retest dates must be stamped on the cylinder.

The tare or stencil weight of the cylinder is an arbitrary value that includes the combined weight of the cylinder proper, porous filling, valve, and solvent, but does not include the removable valve protection cap, if any. The specification sets the maximum amounts of solvent that may be added to an acetylene cylinder. These values range from 35 to 40% of the volume of the cylinder shell (measured by its water capacity), depending on the porosity of the filler.

The Bureau of Explosives also requires and rigidly enforces its regulation that when an acetylene cylinder is filled, its internal pressure may not exceed 250 psig at 70°F.

Filling Cylinders with Acetylene. The filling of acetylene cylinders requires the compression of acetylene to pressures of about 300 psig. The technique calls for careful design and construction of cylinder-charging plants, taking into account all hazard factors. Acetylene is compressed by standard-type compressors, which are usually run at slightly lower than normal speeds. Considerable caution is exercised to be sure that adequate and constant intermediate cooling and aftercooling are maintained. All piping, valves, and fittings carrying acetylene at pressures in excess of 15 psig are heavily constructed to withstand the maximum possible decomposition force to which the acetylene within might subject them.

The contents of charged cylinders are determined by weight. Each cylinder is also checked for any possible valve or fuse-plug leaks. In addition, a constant run-

ning check is made of cylinders picked at random to make certain that the 250 psig pressure at 70°F limitation of the Interstate Commerce Commission is not exceeded.

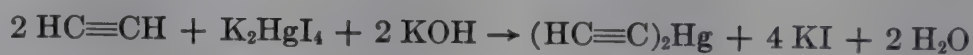
Analysis

Acetylene can be detected in very slight traces by passing the gas through Ilosvay's solution containing a cuprous salt in ammoniacal solution. The presence of acetylene is indicated by a pink or red coloration caused by the formation of copper acetylide, Cu_2C_2 . The same method can be used for the quantitative determination of acetylene in higher concentrations; the copper acetylide is measured colorimetrically or gravimetrically.

The quantitative determination of traces of acetylene can best be accomplished by gas chromatography, which permits an accurate analysis of quantities much less than one part per million. High concentrations of acetylene can be determined volumetrically by absorption in fuming sulfuric acid, by reaction with silver nitrate in solution and titration of the nitric acid formed, or by fractionation in a column of the Podbielniak or Millan type.



Ammonia and hydrogen sulfide interfere with the silver nitrate method which is less accurate than the sulfuric acid absorption method. Acetylene and monosubstituted acetylenes may also be determined by means of potassium mercuric iodide and potassium hydroxide in methanol solution whereby the excess potassium hydroxide is back-titrated (64).



The analysis of acetylene for common impurities includes the determination of phosphorus, sulfur, and nitrogen compounds which are always present in the crude gas derived from calcium carbide. Hydrogen sulfide and phosphine can be detected in concentrations as low as 10 parts per million by the brown to black discoloration of moist silver nitrate paper. The quantitative determination of phosphorus and sulfur can be achieved by oxidation with calcium or sodium hypochlorite. Phosphine and hydrogen sulfide present in the gas are oxidized to phosphate and sulfate and are measured gravimetrically as phosphomolybdate and barium sulfate, respectively. Ammonia is determined by the Nessler method after absorption in dilute hydrochloric acid. Oxygen can be determined by absorption in alkaline pyrogallol after the acetylene has been removed by fuming sulfuric acid.

The analysis of purified hydrocarbon-derived acetylene is primarily concerned with the determination of other unsaturated hydrocarbons. Besides chemical analysis, physical analytical methods are employed, such as infrared and ultraviolet absorption, mass spectroscopy, and gas chromatography.

Uses

The annual production of acetylene in the United States is about 910 million pounds (1960). Of this quantity, approximately 770 million pounds (85%) is consumed by the chemical and allied industries in the manufacture of vinyl chloride, neoprene, acrylonitrile, trichloroethylene, perchloroethylene, and other miscellaneous acetylene derivatives. The remaining 140 million pounds (15%) is consumed in com-

combination with either oxygen or air in such nonchemical producing applications as metal welding (see Welding), cutting, and scarfing (65). Illumination, which was once the principal use of acetylene, has been largely displaced by incandescent lamps. However, the highly luminescent acetylene flame still finds limited use in certain marine and temporary or emergency lighting applications. The estimated industrial consumption of acetylene for these applications is shown in Table 11.

Table 11. Industrial Consumption of Acetylene (1960)

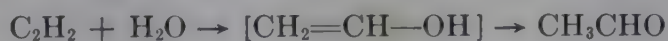
Uses	Million pounds	Percent of total
vinyl chloride	255	28.0
neoprene	175	19.2
acrylonitrile	120	13.1
trichloroethylene	81	8.9
perchloroethylene	9	1.0
vinyl acetate	65	7.2
miscellaneous chemical (eg, acrylates, Reppe chemicals)	65	7.2
<i>total chemical</i>	770	84.6
nonchemical	140	15.4
<i>grand total</i>	910	100.0

Certain olefinic materials, particularly ethylene and propylene, compete with acetylene in the manufacture of many of the major products listed in Table 11, except for neoprene. Ethylene competes in the production of vinyl chloride, acrylonitrile, perchloroethylene, and acrylates. Recently, propylene has started to compete with acetylene as a raw material for the production of acrylonitrile. However, on an overall basis, the percentage of the acetylene-derived products produced from acetylene has not varied greatly in recent years and has been about 70–75%.

Similarly, in nonchemical uses, acetylene-welding gas has encountered competition from propane–butane mixtures, which sell more cheaply.

The high chemical reactivity of acetylene has enticed investigators throughout the world to use it as a raw material for the most diverse organic compounds. The value of acetylene for this purpose is due to two fundamental characteristics; first, the ease with which the triple bond undergoes addition reactions, and second, the ability of the methine hydrogens to be substituted.

Acetaldehyde. One of the oldest commercial uses of acetylene is its reaction with water in the presence of sulfuric acid and mercuric salts to give acetaldehyde.



The postulated intermediate addition product, the unstable vinyl alcohol, is the simplest illustration of the *vinylation* reaction. The production of acetaldehyde by this method is in use abroad but in the U.S. acetaldehyde from acetylene is confined to that obtained as a by-product in connection with the manufacture of chloroprene and acrylonitrile. Both of these involve reaction of acetylene in an aqueous phase. This accounts for no more than 5% of the total U.S. acetaldehyde production. Currently, acetaldehyde is manufactured from ethyl alcohol or liquid petroleum fractions by dehydrogenation or oxidation (see Acetaldehyde).

Vinyl Chloride. Vinyl chloride is one of the most important monomers used in industrial polymerizations. Vinyl chloride is prepared from acetylene by reaction

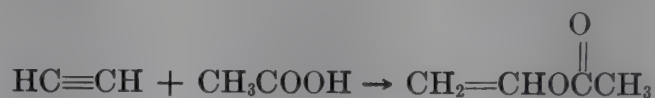
with hydrogen chloride in the vapor phase at a reaction temperature of 150–250°C in the presence of a contact catalyst, such as mercuric chloride on charcoal.



Approximately 60% of the total annual production of vinyl chloride in the U.S. is made from acetylene. The remainder is made by the dehydrochlorination of ethylene dichloride (obtained from ethylene) to yield vinyl chloride and by-product hydrogen chloride. The selection of the process for manufacture depends primarily on price, availability, and purity of raw materials, and, in the case of the ethylene dichloride process, the favorable economic disposal of the by-product, hydrogen chloride.

The major consumption of vinyl chloride is in the manufacture of polyvinyl chloride (PVC) resins, which are used in molding and extrusion, film and sheeting, floor coverings, textile and paper coatings, and other miscellaneous applications (see Vinyl compounds).

Vinyl Acetate. Vinyl acetate is produced by the vapor phase addition of acetic acid to acetylene at 180–200°C over a contact catalyst, such as cadmium, zinc, or mercury salts deposited on charcoal.



Vinyl acetate is also produced by the thermal cracking of ethylidene diacetate, obtained from acetaldehyde and acetic anhydride. However, about 85% of the U.S. vinyl acetate capacity is based on acetylene.

The major polymer products made from vinyl acetate are polyvinyl acetate (homopolymers and copolymers for latex paints, adhesives, and textile finishes), polyvinyl alcohol (adhesives, textile sizing, and protective colloid), polyvinyl butyral (safety glass laminate), and vinyl chloride–vinyl acetate copolymers for a variety of uses from film and sheeting to such molded articles as sound records (see Vinyl compounds).

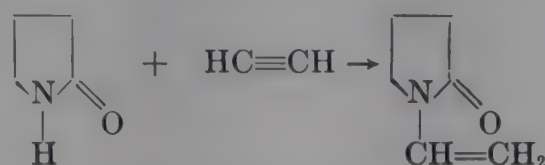
Acrylonitrile. Acrylonitrile was first prepared by the dehydration of acrylamide and by the dehydration of ethylene cyanohydrin. The latter reaction was the chief method for the commercial preparation of acrylonitrile prior to World War II. Recently, however, the manufacture of acrylonitrile from acetylene has assumed major commercial significance, and approximately 70% of the present U.S. capacity of acrylonitrile is based on this reaction.

The addition of hydrogen cyanide to acetylene can be accomplished in either the liquid or vapor phase, $\text{HC}\equiv\text{CH} \rightarrow \text{CH}_2=\text{CHCN}$.

Recently, commercial propylene–ammonia processes have entered the acrylonitrile field and are based on the catalytic vapor phase reaction of propylene, ammonia, and air to yield acrylonitrile with minor amounts of acetonitrile and hydrogen cyanide as by-products. Although such processes have an obvious raw material economic advantage and constitute a threat to acetylene processes for acrylonitrile, this must be proved in actual plant performance.

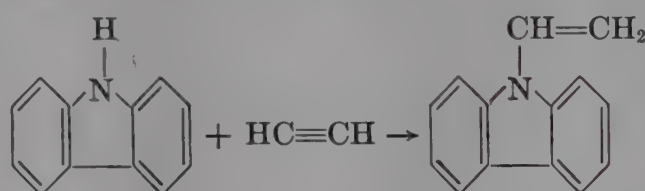
About 70% of the total U.S. acrylonitrile production goes into fibers (see Acrylic and modacrylic fibers). The second major use of acrylonitrile is in the production of nitrile rubbers (see Elastomers, synthetic; Acrylonitrile).

Vinylpyrrolidone. Carboxylic acid amides, having only one hydrogen atom on the nitrogen, $RCONHR'$, react with acetylene under pressure at temperatures from 130–160°C and in the presence of their alkali metal salts as catalysts to give the corresponding *N*-vinyl derivatives. However, of the vinylamides prepared in this manner, only 1-vinyl-2-pyrrolidone (General Aniline & Film Corp.) has achieved commercial production in this country.



The polymers and copolymers of vinylpyrrolidone are used in such diverse applications as adhesives, beverage clarification, cosmetics, coatings, detergents, inks, lube-oil additives, pharmaceutical preparations, synthetic fibers, and textile finishing, sizing, and dyeing. These polymers and copolymers are available in the U.S. under such designations as Plasdone, PVP, PVP/VA, Polyclar, Polecrons (General Aniline & Film Corp.), and Acryloids (Rohm & Haas).

Vinyl Amine. Primary and secondary aliphatic amines, as well as such aromatic amines as aniline and ethyl aniline, give no uniform products on reaction with acetylene. However, less basic secondary aromatic amines, such as carbazole and diphenylamine, yield the corresponding *N*-vinyl derivative with acetylene under pressure at temperatures between 150–200°C and in the presence of alkali, zinc, or cadmium oxides, or their salts with organic acids as catalysts.



Of the vinylamines, *N*-vinylcarbazole attained the greatest industrial importance during World War II when substantial quantities of polyvinylcarbazole were produced as a replacement for mica in the field of electrical insulation.

Vinyl Ethers. Alcohols, including polyols and phenols, react with acetylene under pressure at temperatures between 120–180°C in the presence of alkaline catalysts to give vinyl ethers.



Vinyl ethers are easily polymerized with such acidic catalysts as boron trifluoride and aluminum chloride. Furthermore, polymers of varying degrees of crystallinity can be obtained by the use of boron trifluoride etherate or transition metal halide-alkylaluminum compounds and related stereospecific catalysts. Depending upon the vinyl ether employed and the polymerization procedure, the poly(vinyl alkyl ethers) may vary from balsamlike materials to solids with a high degree of crystallinity. Notwithstanding their diversity of properties and applications, the poly(vinyl alkyl ethers) have yet to achieve wide commercial acceptance.

The alkyl vinyl ethers can be copolymerized with a variety of polymerizable unsaturates by free-radical catalysts. Copolymers of alkyl vinyl ethers and maleic anhydride can be formed by free-radical initiation. The methyl vinyl ether-maleic anhydride copolymer (GANTREZ AN) is produced by General Aniline & Film Corp.

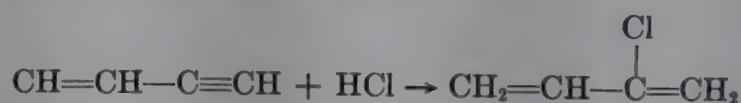
The copolymer and its derivatives find use in detergent formulations, cosmetic preparations, and textile sizing and finishing.

Self-Addition. One of Nieuwland's many significant contributions to acetylene chemistry was his discovery that acetylene could be converted to vinylacetylene.



By passing acetylene through an aqueous solution of cuprous chloride, ammonium chloride, and hydrogen chloride at 50–60°C, vinylacetylene is obtained, together with divinylacetylene. The reaction is generally carried out in the absence of oxygen or in the presence of antioxidants.

The most important use of vinylacetylene is in the synthesis of 2-chloro-1,3-butadiene (*chloroprene*), which is then polymerized,

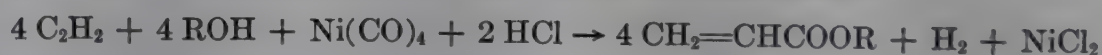


to give *neoprene* (Du Pont). Neoprene has good resistance to oil, grease, sunlight, ozone, heat, and flame and is the only major commercial product produced exclusively from acetylene (see Elastomers, synthetic).

Carbonylation. Reppe (46) discovered that carbon monoxide and an aliphatic alcohol or water react with acetylene in the presence of nickel carbonyl and hydrogen chloride or nickel salts as catalysts to give either acrylic acid or its esters.



Reppe developed two processes for the preparation of acrylic acid and its esters. One was a stoichiometric reaction employing nickel carbonyl as the source of carbon monoxide under mild conditions of temperature and pressure.

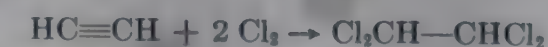


The other employed carbon monoxide, acetylene and an alcohol at 150–180°C and pressures of about 30 atmospheres in the presence of nickel bromide or nickel iodide as catalysts, $\text{C}_2\text{H}_2 + \text{CO} + \text{ROH} \rightarrow \text{CH}_2=\text{CHCOOR}$.

In the United States, Rohm & Haas has developed an improved catalytic process based upon the discovery that the reaction of acetylene, carbon monoxide, and alcohol can be superimposed upon the nickel carbonyl reaction, under mild conditions of temperature and pressure, thereby employing only small quantities of nickel carbonyl as the catalyst (66). Also, Dow Badische, jointly owned by Dow Chemical and Badische Anilin- & Soda-Fabrik, produces acrylate esters by esterification of acrylic acid made by a Reppe catalytic process involving acetylene, carbon monoxide, and water. Acrylic esters are also made from the reaction of ethylene cyanohydrin and an alcohol (Union Carbide) and by the addition of an alcohol to propiolactone (Celanese).

The acrylate polymers and copolymers are used in paints, leather, paper, polished rubbers, and plastics (see Acrylic acid and derivatives).

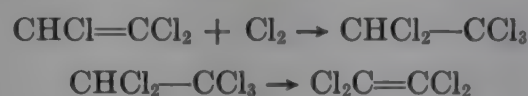
Chlorination. The addition of chlorine to acetylene to form tetrachloroethane, which is then dehydrochlorinated to *trichloroethylene*, constitutes the fourth largest chemical end use for acetylene.



Trichloroethylene is also produced by thermal or catalytic cracking of tetrachloroethane obtained from ethylene (67).

The most important commercial use for trichloroethylene is for vapor degreasing, which involves the removal of grease, fats, and oils from metals by the action of the pure solvent as it condenses on the cold material to be cleaned. Trichloroethylene is also used as an extraction solvent, as a freezing point depressant, in textile processing, in paper dewaxing, in phosphatizing, and in painting. About 90% of trichloroethylene production is based on acetylene. The remainder is derived from the chlorination of ethylene dichloride followed by cracking.

Trichloroethylene is used also as an intermediate for the preparation of *perchloroethylene*. By chlorination, trichloroethylene is converted to pentachloroethane from which perchloroethylene is obtained by dehydrochlorination.



This process has been simplified by passing a mixture of acetylene and chlorine, in the presence of an inert diluent, over a contact catalyst at 250–400°C to yield perchloroethylene, together with other chlorinated hydrocarbons. Alternatively, perchloroethylene is obtained by the controlled combustion of a mixture of acetylene and chlorine at temperatures of 600–950°C in the absence of a catalyst (68).

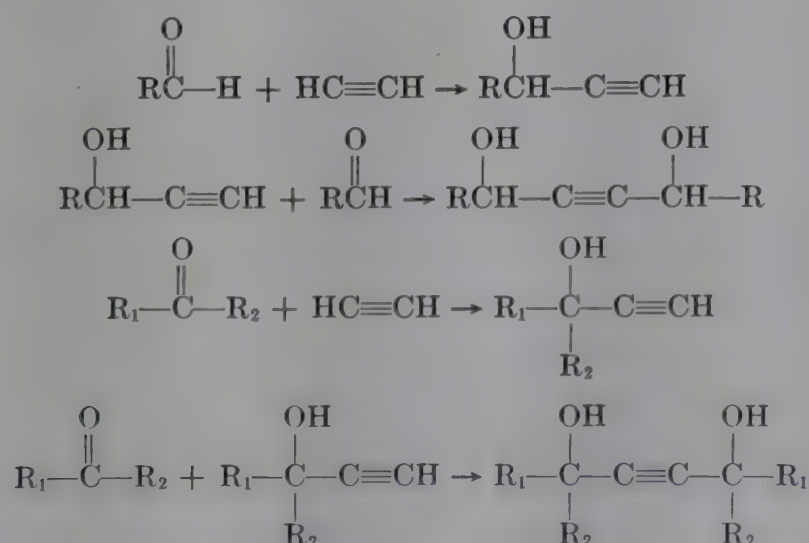
Perchloroethylene is used in drycleaning, in metal degreasing, and as a solvent (see Chlorocarbons and chlorohydrocarbons).

Hydrogenation. Acetylene can be either partially or completely hydrogenated by employing various platinum, palladium, and nickel catalysts and gives either ethylene or ethane.



During World War II, appreciable quantities of ethylene were produced in Germany from acetylene. However, ethylene is currently produced both in this country and abroad by the thermal cracking of petroleum fractions.

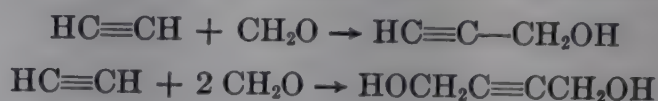
Ethynylation. The term “ethynylation” is used to designate the addition of acetylene to an aldehyde or ketone to give acetylenic alcohols as indicated in the following equations:



In ethynylations the triple bond of the acetylene is maintained intact. The reaction of acetylene with aldehydes, according to the Reppe process, is accomplished at

a temperature of about 100°C and a pressure of 3 atm or higher in the presence of cuprous acetylide deposited on a suitable carrier as the catalyst. The reaction of acetylene with ketones is carried out in ethers, acetals, or other inert solvents in the presence of sodium or potassium hydroxide, sodamide, potassium *t*-butoxide, or other alkali or alkaline earth oxides as condensing agents.

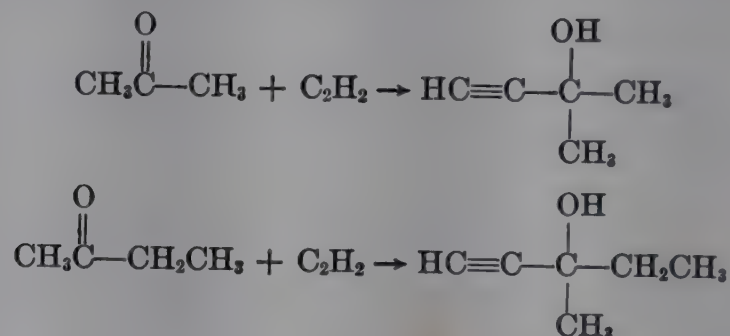
Of the reactions of acetylene with aldehydes, its reaction with formaldehyde to yield 2-propyne-1-ol (propargyl alcohol) and 2-butyne-1,4-diol is the only one to achieve industrial importance in this country (General Aniline & Film Corp.).



Propargyl alcohol and its derivatives are useful as corrosion inhibitors, in soil fumigant formulations, and as intermediates in the synthesis of pharmaceuticals and agricultural chemicals.

Butynediol is used in electroplating baths, corrosion inhibitors, paint and varnish remover formulations, and defoliation. In addition, butynediol is the starting material for the industrial manufacture of 2-butene-1,4-diol, 1,4-butanediol, γ -butyrolactone, 2-pyrrolidone, and 1-methyl-2-pyrrolidone.

Methylbutynol and methylpentynol, prepared from the reaction of acetylene with acetone and 2-butanone, respectively, have achieved commercial production in this country (Air Reduction Co., Inc.).



These products are used in the production of hypnotics and tranquilizers, and as intermediates for vitamin A, ionones, and other isoprenoid chemicals (see Alcohols, unsaturated).

Economics

Economic comparisons for producing acetylene from calcium carbide and from hydrocarbons are difficult to make and are complicated by such factors as raw material costs, transportation, utilities, location of consumers, volume, and by-product use.

Calcium carbide yields high-purity acetylene which is suitable for most chemical uses with little or no purification. The hydrocarbon processes, however, produce a cracker stream containing relatively low concentrations of acetylene, together with impurities, which must be purified. This represents one of the major cost factors in the hydrocarbon process. The availability of cheap electric power is an important economic factor in producing calcium carbide. Furthermore, transportation costs dictate that calcium carbide plants be located near supplies of limestone and coal (for coke).

The utilization of by-products is another important economic factor in arriving at acetylene manufacturing costs. Hydrogen, carbon monoxide, and nitrogen are by-

products from a hydrocarbon-acetylene plant. These products are used to make ammonia and methanol; hence, the cost of acetylene is influenced by the value taken for these coproducts. Natural-gas price trends are also an important factor in acetylene economics. Natural-gas prices are rising presently at an average rate of 2% each year. The importance of gas prices in acetylene manufacture is accentuated by the fact that the hydrocarbon raw material may represent as much as half of the total manufacturing cost. Therefore, in view of the complexity of production and distribution economics involved, carbide acetylene may be more economical in one situation and hydrocarbon-acetylene in another.

Similarly, whether or not acetylene should be purchased from a supplier located next door or manufactured by the consumer is determined by such factors as volume, location, length of contract, take-or-pay clauses, and economics of the derived product.

Merchant acetylene from calcium carbide generally sells between 12½–14¢/lb (1962) depending on the location of the consumer, although the price may be either lower or higher than this range, depending on conditions. Almost all of the hydrocarbon acetylene in the U.S. is captive, hence, no comparable market price of hydrocarbon acetylene is significant.

A summary of the costs for producing acetylene by various routes as a function of annual production rate has been given by Lobo (69).

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ACETYLENE BLACK. See Carbon black under Carbon.

ACETYLENE DICHLORIDE (1,2-dichloroethylene), $\text{ClCH}=\text{CHCl}$. See Chlorocarbons and chlorohydrocarbons.

ACETYLENE TETRABROMIDE (1,1,2,2-tetrabromoethane), $\text{CHBr}_2\text{CHBr}_2$. See Bromine compounds.

ACETYLENE TETRACHLORIDE (1,1,2,2-tetrachloroethane), $\text{CHCl}_2\text{CHCl}_2$. See Chlorocarbons and chlorohydrocarbons.

ACETYLENIC ALCOHOLS. See Alcohols, unsaturated.

ACETYLENIC GLYCOLS. See Alcohols, unsaturated.

ACETYL FLUORIDE, CH_3COF . See Fluorine compounds, organic.

ACETYLIDES. See Acetylene; Carbides.

ACETYL PEROXIDE, $(\text{CH}_3\text{CO})_2\text{O}_2$. See Peroxides and peroxy compounds, organic.

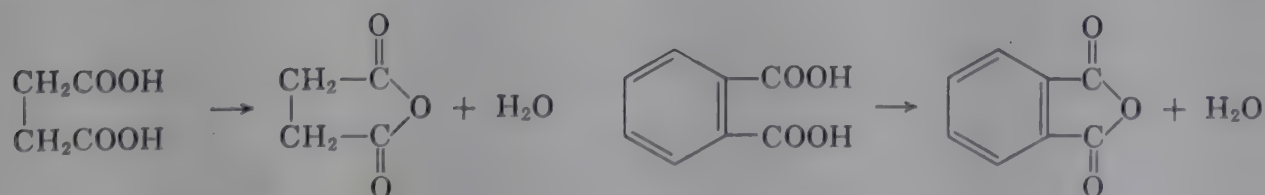
ACETYLSALICYLIC ACID, $o\text{-CH}_3\text{COOC}_6\text{H}_4\text{COOH}$. See Analgesics and antipyretics; Salicylic acid.

ACID ANHYDRIDES

Acid anhydrides are compounds that react with water to form acids only. In inorganic chemistry the term is applied to most oxides of nonmetals. Most organic acid anhydrides have the type formula $(\text{RCO})_2\text{O}$, in which the two R groups are usually the same, and are named from the corresponding acids (see Ethanoic acid; Propionic acid; etc). They may be thought of as acid derivatives in which one molecule of water has been removed from two carboxyl groups,

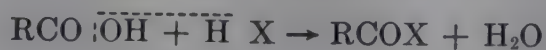


and severe dehydrating conditions do indeed produce this reaction. However, heat alone does not produce very satisfactory results except in converting dicarboxylic acids such as succinic and phthalic acids to the easily formed 5- or 6-membered cyclic anhydrides.

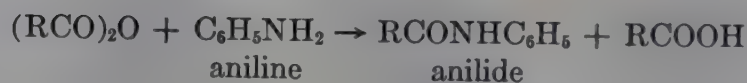
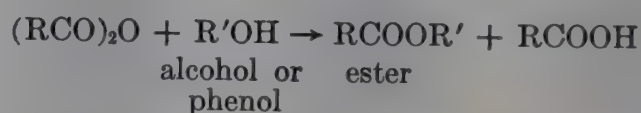
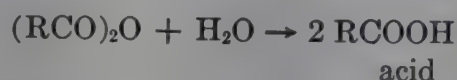


In these cases, favorable spatial relations between the carboxylic acid groups and the stability of the anhydride rings are conducive to the elimination reaction. These factors are absent with ordinary acids.

Ketenes, $\text{RCH}=\text{CO}$ or $\text{R}_2\text{C}=\text{CO}$, may be considered intramolecular anhydrides as they are formed by removal of one molecule of water from one molecule of acid, rather than from two molecules of acid. They show many of the reactions of acid anhydrides, but are usually discussed as a separate class of compounds (see Ketenes). Mixed acid anhydrides are also known, the most important being acid halides (qv), for example,

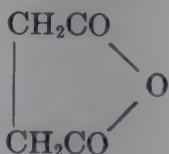
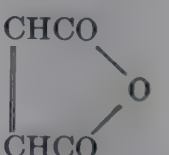
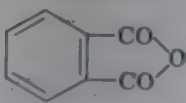


Ordinary (intermolecular) organic acid anhydrides (see Table 1 for examples) are neutral liquids or solids which boil at higher temperatures than the corresponding acids. The liquids are irritating to the eyes, nose, and throat. Anhydrides are relatively soluble in organic solvents. Acid anhydrides are used for introducing the $\text{RCO}-$ radical (acyl group) in the place of hydrogen atoms attached to oxygen, sulfur, nitrogen, or, rarely, carbon atoms (see Esterification).



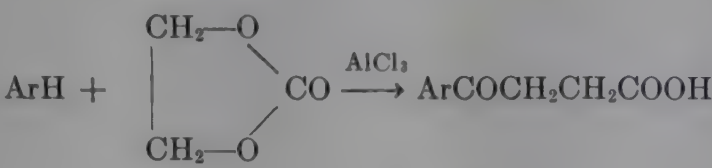
They are used when the acid itself reacts too sluggishly, and are preferred to the more active, but more expensive, acid chlorides in the manufacture of such products as cellulose acetate, acetylsalicylic acid (aspirin), and plastics made by esterification processes.

Table 1. Important Organic Acid Anhydrides

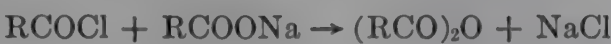
Name	Formula	Mp, °C	Bp, °C	d_4^{20}
acetic anhydride	$(\text{CH}_3\text{CO})_2\text{O}$	-73.1	140.0	1.0871 ₄ ¹⁵
propionic anhydride	$(\text{C}_2\text{H}_5\text{CO})_2\text{O}$	-45	169.3 (166)	1.0336 ₄ ²
butyric anhydride	$(\text{CH}_3\text{CH}_2\text{CH}_2\text{CO})_2\text{O}$	-75.0 (-56.1)	198	0.9946
succinic anhydride		119.6	261	1.104
maleic anhydride		53 (57-60)	202 (196)	0.934
benzoic anhydride	$(\text{C}_6\text{H}_5\text{CO})_2\text{O}$	42	360	1.1989 ₄ ¹⁵
phthalic anhydride		130.8	284.5 subl	1.527 ⁴

NOTE: Specific gravity is given as d_4^{20} unless otherwise indicated.

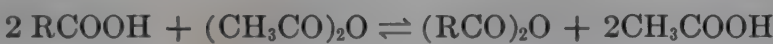
The lower anhydrides react with water more rapidly than the higher, which require long heating because of their slight solubility. The more active anhydrides can be used to remove water from salt hydrates or in reactions such as nitrations and sulfonations. Acid anhydrides also undergo the Perkin reaction with aromatic aldehydes to yield, usually, α,β -unsaturated acids. In the Friedel-Crafts reaction (qv), acid anhydrides may be used as donors of the acyl group to form aromatic ketones. Of particular utility is the use of cyclic anhydrides; eg, the use of succinic anhydride to form β -aroylpropionic acids,



The best-known process for making anhydrides is to condense an acid chloride with the sodium salt of the acid,



In practice the acid chloride is not separately prepared. Instead, the sodium salt is treated with just enough phosphorus oxychloride, sulfuryl chloride, or the like, to convert half of the salt to acid chloride, whereupon the condensation follows. Another preparation of anhydrides which proceeds in excellent yield is the exchange of acids with acetic anhydride,



The reaction can be driven to completion by distilling out the acetic acid. This is a useful method for preparing benzoic anhydride. In a more recent process, catalytic addition of a carboxylic acid to acetylene yields an ethylidene diester, $\text{CH}_3\text{CH}(\text{OOCR})_2$, which produces an anhydride and acetaldehyde when heated. Again, the addition of a carboxylic acid to ketene, made by cracking acetone, gives the anhydride directly,



Maleic and phthalic anhydrides are manufactured by the catalytic vapor-phase oxidation of benzene and naphthalene, respectively.

“Acid Anhydrides” in *ECT* 1st ed., Vol. 1, pp. 126–128, by O. C. Dermer, Oklahoma Agricultural and Mechanical College.

ACID-BASE SYSTEMS

Early ideas about acids and bases were restatements of certain physical and chemical properties. For acids these properties included a sour taste, the ability to change the color of certain vegetable dyes, and the production of effervescence on addition to chalk. Bases opposed or neutralized acids, and salts resulted from such neutralizations.

The first structural theory of acidity was advanced by Lavoisier. He considered the element oxygen to be the acidifying principle, naming it from the Greek for acid-former. Nonmetals like sulfur and phosphorus on combustion in oxygen produced acids. A metal on combination with oxygen yielded a metallic calx or base. This theory persisted almost into the middle of the nineteenth century, owing largely to

the influence of Berzelius. It was the first of the one-particle theories of acid-base behavior. It was disproved by Davy's work on the element chlorine. However, Lux and others, only some twenty years ago (1), as a result of investigations of reactions in fused glasses and other molten salts, have revived a very similar theory, for they felt it necessary to define a base as a substance which can yield an oxide ion:



(The temperatures are those involved in ceramic reactions.)

Hydrogen Acids

The Lavoisier theory required that hydrochloric acid contain oxygen. Davy demonstrated that it did not. He suggested in turn that acidity might be associated with hydrogen, which for acids was playing the role of the metal in the corresponding salts. Liebig supported this view, reinforcing it with examples from organic chemistry. Thus, he wrote, "Acids are . . . hydrogen compounds in which the hydrogen may be replaced by metals. Neutral salts are compounds of the same class wherein the hydrogen has been replaced by a metal." This is the genesis of the most successful of the various one-particle theories of acid-base behavior.

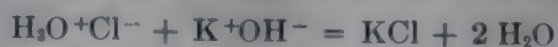
In 1884 Arrhenius advanced an explanation of acid-base behavior in water as a part of his general theory of ionization. Acids were substances which in water dissociated into hydrogen ions (protons) and anions. Bases dissociated into cations and hydroxyl ions. A quantitative measure of acid strength could be drawn from a mass-action constant based on the electrical conductivity of the solution in question. Neutralization was the reaction between protons and hydroxyl ions. The hydrolysis of salts, the behavior of acid-base indicators, and the course of acid-base titrations were quantitatively explained. The mass-action constants (now known as classical dissociation constants) are still useful today for formulating equilibria in water involving weak electrolytes, such as acetic acid:



$$K_A = \frac{[\text{H}^+][\text{OAc}^-]}{[\text{HOAc}]}$$

(The hydrogen ion does not now refer to an actual proton, but is a symbol for some solvated species.)

From a conceptual point of view the Arrhenius theory of acidity faced difficulties rather soon. The chemical proton had an estimated radius of approximately 10^{-8} cm, whereas the physical proton, based on nuclear scatter, was five orders of magnitude smaller. The insistence on electrolytic conductance as demonstration of acidity ran afoul of experiments by Vorländer (2), who successfully titrated aniline with hydrogen chloride in benzene, a medium in which hydrogen chloride does not conduct current appreciably. From the work of Franklin and his collaborators (3), it was clear that ammonium salts, when dissolved in liquid ammonia, behaved very much like strong acids in water, and alkali metal amides in ammonia resembled alkali metal hydroxides in water. In fact, an ammonium chloride solution in liquid ammonia can be titrated with potassium amide to a successful end point, using phenolphthalein as the indicator, very much like the corresponding titration in water:



The particle H_3O^+ , called the hydronium ion, has been demonstrated to exist in the crystalline monohydrate of perchloric acid, $\text{HClO}_4\cdot\text{H}_2\text{O}$, which is isomorphous with crystalline $\text{NH}_4^+\text{ClO}_4^-$ (4); and proton magnetic resonance measurements of the solid monohydrates of nitric, perchloric, and sulfuric acids yield almost identical proton frequency patterns (5). In solution, however, hydronium ions may be—and undoubtedly are—much more heavily solvated.

In 1923 Brønsted (6) proposed a generalized definition of acids and bases which succeeded in coordinating the results of catalytic studies, indicator measurements, and neutralization and displacement reactions in solution. An acid is a substance which is capable of giving up a proton to a base. A base is a compound which can take up a proton from an acid:



The mass-action constants for these reactions take the form

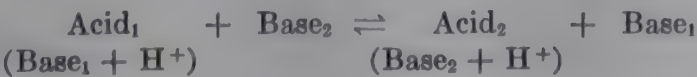
$$K_A = \frac{a_{\text{H}^+} a_{\text{Base}}}{a_{\text{Acid}}}; \quad K_B = \frac{a_{\text{Acid}}}{a_{\text{H}^+} a_{\text{Base}}}; \quad K_A = \frac{1}{K_B}$$

and are expressed in terms of the activities of the reacting particles. Such a definition is a universal one (at least for hydrogen acids) and is independent of solvent. The equations state that for every acid there will be a particle which contains one proton less. Such a particle is called the conjugate base of the acid. Correspondingly, the addition of a proton to a molecule or ion will form an acid, which is called the conjugate acid of the base. The concept of acids and conjugate bases is not dependent upon any particular structure, or electric charge, except for the presence of a transferable proton. Table 1 includes a variety of such acids and bases.

Table 1. Acids and Bases

Acids	Conjugate bases	Bases	Conjugate acids
HCl	Cl^-	$\text{C}_6\text{H}_5\text{NH}_2$	$\text{C}_6\text{H}_5\text{NH}_3^+$
NH_4^+	NH_3	HCl	H_2Cl^+
NH_3	NH_2^-	$\text{HC}_2\text{H}_3\text{O}_2$	$\text{H}_2\text{C}_2\text{H}_3\text{O}_2^+$
H_3O^+	H_2O	N_2H_4	N_2H_5^+
H_2O	OH^-	N_2H_6^+	$\text{N}_2\text{H}_6^{2+}$
OH^-	O^{2-}	$(\text{CH}_3)_2\text{O}$	$(\text{CH}_3)_2\text{OH}^+$
$\text{HC}_2\text{H}_3\text{O}_2$	$\text{C}_2\text{H}_3\text{O}_2^-$	$(\text{CH}_3)_2\text{CO}$	$(\text{CH}_3)_2\text{COH}^+$
$\text{Al}(\text{H}_2\text{O})_6^{3+}$	$\text{Al}(\text{H}_2\text{O})_5\text{OH}^{2+}$		
$\text{CO}(\text{NH}_2)_2$	$\text{CO}(\text{NH}_2)\text{NH}^-$	$\text{CO}(\text{NH}_2)_2$	$\text{CO}(\text{NH}_2)(\text{NH}_3)^+$
H_2	H^-		
HClO_4	ClO_4^-		

The original Brønsted definition is incapable of experimental realization. In order to demonstrate the acidity of an acid, a base from another system must react with it, with transference of a proton:



In this equation $\text{Acid}_1\text{--Base}_1$ represents one conjugate pair, and $\text{Acid}_2\text{--Base}_2$ represents a second pair. The mass-action constant, written for convenience in terms of concentrations, takes the form

$$K = \frac{[\text{Acid}_2][\text{Base}_1]}{[\text{Acid}_1][\text{Base}_2]}$$

This constant can be expressed as the ratio of two acidity constants,

$$K = \frac{K_{a1}}{K_{a2}} = \frac{[\text{Base}_1][\text{H}^+]/[\text{Acid}_1]}{[\text{Base}_2][\text{H}^+]/[\text{Acid}_2]}$$

emphasizing the point that the practical measurement of acidity (or basicity) is a relative measurement—that is, the acidity of Acid_2 is measured relative to that of Acid_1 , to which is assigned an arbitrary value (usually unity). This implies in turn that a hydrogen-containing compound could be made to transfer a proton if a sufficiently strong base were found, and that even a very weak base might be made to take up a proton from a sufficiently strong acid. Where the reference conjugate acid-base pair is derived from a solvent which is itself both acidic and basic (amphiprotic), this concept is easy to see. Hydrogen gas in water is an extremely weak acid, much too weak to be measured. Hydride ion is a very strong base, and reacts with water virtually completely:



Again, HCl in water is a strong acid, and chloride ion is a weak base:



On the other hand, in concentrated sulfuric acid HCl is a very weak acid, and chloride ion is a very strong base. (Recall the traditional laboratory preparation of hydrogen chloride gas from sodium chloride and concentrated sulfuric acid.) In liquid ammonia, which is a basic solvent, benzoic acid reacts very extensively—as completely as any other acid:



In glacial acetic acid, which is more acidic and less basic than water, it does not react to any marked extent:



In pure sulfuric acid, which is extremely acidic and much less basic than acetic acid, it does not function as an acid, but rather, because of its oxygen atoms, it now behaves like a base:

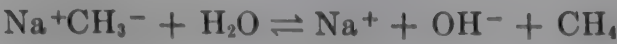


The more acidic the solvent, the wider will be the range of substances which will behave like bases in that solvent. The more basic the solvent, the greater will be the range of substances which can be made to show acidic properties.

In amphiprotic solvents there are limits to the acids and bases which can be tolerated. If the solute acid is stronger than the solvent acid, reaction will take place, destroying the solute acid and producing the acid of the solvent (the lyonium ion):



Similarly, if a solute base is stronger than the solvent base, reaction will occur, producing the base of the solvent (the lyate ion):



The self-ionization constant or autoprotolysis constant of such a solvent is a measure of the range of acid strengths which can be tolerated in it. Thus, for water,



$$K_{\text{W}} = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}$$

$$K_{\text{H}_3\text{O}^+} = \frac{[\text{H}^+][\text{H}_2\text{O}]}{[\text{H}_3\text{O}^+]}$$

$$K_{\text{OH}^-} = \frac{[\text{H}_2\text{O}]}{[\text{H}^+][\text{OH}^-]}$$

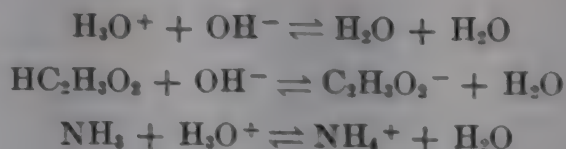
$$K_{\text{W}} = \left[\frac{1}{K_{\text{H}_3\text{O}^+}} \right] \left[\frac{1}{K_{\text{OH}^-}} \right]$$

The self-ionization constant for water can be interpreted as the reciprocal product of the acidity constant for hydronium ion and the basicity constant for hydroxyl ion.

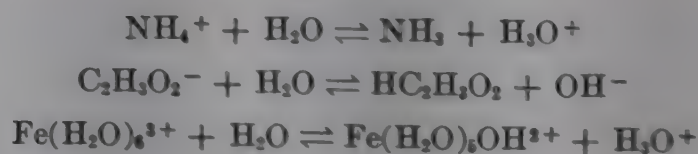
One further consequence of reaction in amphiprotic solvents is the leveling reaction (7). If the reaction is complete between a solute acid and a solvent, producing the solvent acid, the solute acid is said to be leveled—that is, a leveling reaction has taken place. All solute acids above a certain strength will appear to react equally completely with a basic solvent, producing approximately equal yields of the solvent conjugate acid. Thus in dilute solution both HCl and HClO₄ react completely with water, although there is reason to believe that HClO₄ is a much stronger acid than HCl. It is difficult to distinguish between a reaction which is, say, 99.9% complete and one which is 99.999% complete. In a more basic solvent than water—a solvent like liquid ammonia, for example—acids which are weak in water may be leveled, and thus produce an analytically satisfying yield of the solvent acid, ammonium ion. In the same way, in glacial acetic acid, which is a more acidic solvent than water, bases like aniline which are very weak in water are leveled, producing a yield of the solvent base, acetate ion, which can easily be detected.

In the leveling process the original acid becomes transformed to the acid of the solvent, which is a weaker acid. This, after all, is why the reaction took place. A given acid like perchloric acid will furnish a more acidic solution in a nonleveling solvent like acetic acid than in a leveling solvent like water. This means that perchloric acid in glacial acetic acid will react with much weaker bases than will perchloric acid in water. On the other hand, acetic acid will level strong and weak bases (in this case, all bases as strong as or stronger than aniline). A solvent like carbon tetrachloride which has neither acidic nor basic properties to any detectable extent—an aprotic or aprotonic solvent—is one which will tolerate the strongest possible hydrogen acids as well as the strongest possible bases without seriously diminishing their strengths. The widest range of acid-base reactions is therefore found in solvents like benzene and carbon tetrachloride.

All reactions involving acids and bases are themselves acid-base reactions. Thus, the familiar neutralizations,



are reactions in which new acids and bases are formed. In the same vein, the reactions which classically have been called hydrolysis reactions,



are acid-base reactions. The acid ammonium ion is transferring a proton to the base, water, to form a new acid-base pair. The base acetate ion abstracts a proton from water (an acid) to form acetic acid and the base hydroxyl ion. Every acid has an acidity constant, each conjugate base has a basicity constant, and they are related in a simple way to each other. If the reaction between the acid and the base water is written and its mass-action constant is called K_A , and the reaction between the conjugate base and water (now an acid) is written and this mass-action constant is called K_B , then

$$K_A K_B = [\text{H}_3\text{O}^+][\text{OH}^-]$$

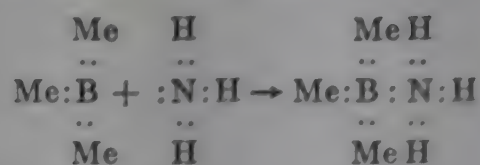
For acetic acid, K_A is identical with the classical ionization constant and K_B has the same value as the traditional hydrolysis constant. For ammonia, K_A is the same as the traditional hydrolysis constant, and K_B is the classical ionization constant. Since the acidity and basicity constants are related to each other in a known fashion, it is not necessary to state both in order to define a given system. By convention the acidity constant of the conjugate acid is used for quantitative descriptions.

Lewis Acids and Bases

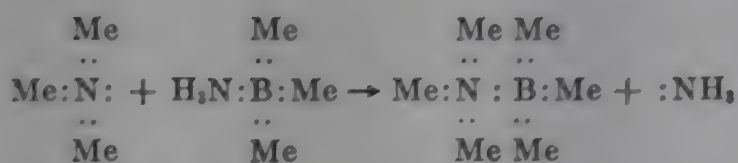
In 1923 G. N. Lewis (8) put forward a definition of acids and bases which was very much wider in scope than that of Brønsted. He proposed that every substance which showed the chemical behavior of an acid or a base be called acid or base, and found from the theoretical side an electronic structural factor which was common to the otherwise bewildering assortment of species which were subsumed under the same phenomenological tent. The experimental criteria for acids and bases were neutralization, reaction with indicators, displacement, and catalysis. The electronic structure which characterized bases was an electron pair available to form a coordinate covalent bond. Acids were substances which would receive one or more pairs of electrons to form such a bond. The list of bases is the same in the Brønsted and Lewis schemes. There is, however, a very much larger group of acids in the Lewis sense. In addition to the hydrogen acids, there are substances like AlCl_3 , SO_3 , SnCl_4 , BF_3 , ZnCl_2 , and AgNO_3 .

The four criteria for acid-base behavior are interpreted below in terms of the Lewis theory.

Neutralization. $B(CH_3)_3$ reacts with NH_3 :

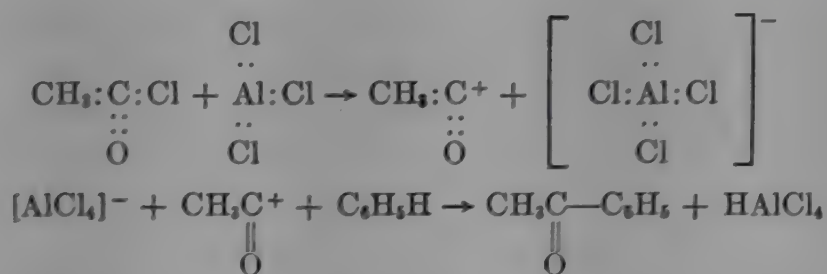


Displacement. A stronger base can displace a weaker base from combination with an acid:



Titration with Indicators. Crystal violet in water is violet. It turns to green and then to yellow as increasing amounts of a strong acid are added. In chlorobenzene the same indicator changes from violet to yellow on addition of $SnCl_4$ or BCl_3 . Addition of bases, like ketones or ethers, will cause the color to change back to violet.

Catalysis. Friedel-Crafts catalysts include $AlCl_3$, $FeCl_3$, and other anhydrous halides:

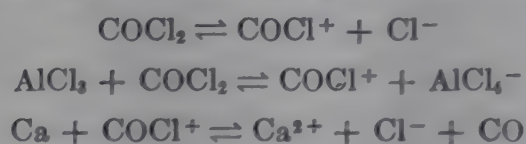


The Lewis system of acids and bases has been extremely useful in coordinating a large number of reactions in solvents which do not involve hydrogen transfer, but do involve typical acid-base behavior. In the absence of the Lewis theory, a different set of reactions would have been written for each solvent (and in fact was), and there would have been no common classification. The work of Germann (9) on phosgene as a solvent illustrates this. Phosgene ($COCl_2$) conducts rather poorly. Calcium metal displaces CO slowly in the solvent:



$AlCl_3$ in phosgene conducts current well, and if calcium is added to this solution there is a very brisk evolution of CO. The addition of KCl (itself insoluble) to the $AlCl_3$ solution (in which it dissolves) causes a marked decrease in the rate of CO evolution when more calcium is added.

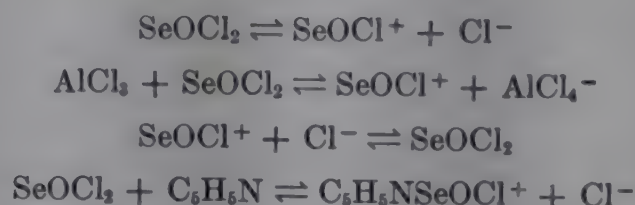
The following equilibria explain the results, in terms of solvent particles:



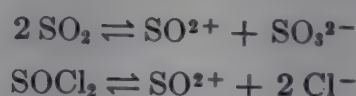
Thus, chlorides are bases in phosgene. The $AlCl_3$ must, however, be recognized as an acid, displacing the weaker acid $COCl^+$ (which is the characteristic solvent acid).

Work by Smith (10) on reactions in $SeOCl_2$ as a solvent involved potentiometric titrations of $SnCl_4$ with pyridine, and conductimetric titrations of acids like SO_3 ,

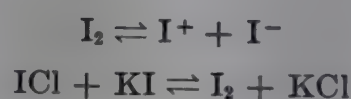
SnCl_4 , FeCl_3 , and AsCl_3 by bases such as pyridine, ammonia, and KCl . Typical reactions included:



Jander (11) showed in similar fashion that in liquid sulfur dioxide, thionyl chloride, SOCl_2 , is an acid, and tetramethylammonium sulfite, $(\text{Me}_4\text{N})_2\text{SO}_3$, is a base:

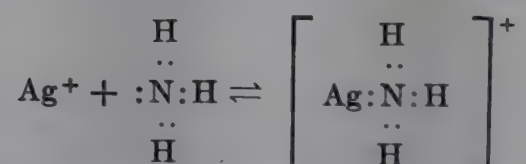


Again, in molten iodine, Jander (12) demonstrated that various iodides are bases, and iodine chloride is an acid:

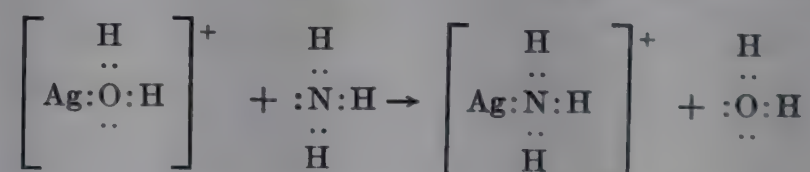


The Lewis theory successfully organizes all these solvent reactions into one group, characterized by the formation of coordinate covalent bonds.

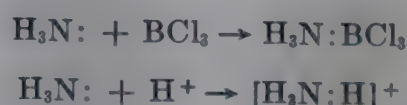
All coordination reactions can be interpreted as acid-base reactions. Thus, for example, the familiar complexation of silver ion by ammonia can be viewed in this way:



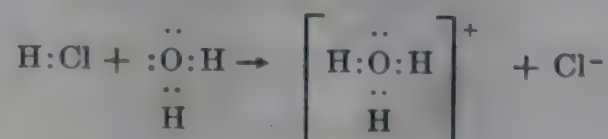
However, care must be exercised in interpreting this reaction as a neutralization reaction. In a solvent like water it is more certainly a displacement reaction:



This brings up the question of hydrogen acids. In a formal sense all protonic acids can be included in the Lewis scheme. There are, however, some difficulties. There are no neutralization reactions for protonic acids in Lewis' sense. One can write



However, the analogy which is suggested here is a false one. There are no free protons for such a reaction. The hydrogen acids can be incorporated in the general Lewis scheme only through displacement reactions:



Neutralization in the experimental and historical sense certainly applies to these acids; but a one-step reaction involving the formation of a single covalent bond, as with gaseous $\text{B}(\text{CH}_3)_3$ and NH_3 , is out of the question.

Another problem in considering protonic acids and nonprotonic acids together is that posed by the hydrogen bond. Undoubtedly, this plays an important part in all hydrogen-ion transfer processes, either through the solvent, or, in aprotic media of low dielectric constant, through the product of the acid-base reaction. There is nothing analogous to this bond, which is generally regarded as electrostatic in nature, in the case of the nonprotonic acids. It has been proposed (13) that neutralization reactions (in the Lewis sense) can take place with hydrogen acids through the mechanism of the hydrogen bond. However, this requires that the hydrogen bond be covalent, rather than coulombic. If it is covalent, then hydrogen is capable of coordinating two groups simultaneously. This has not been observed experimentally.

The Brønsted scheme permits quantitative calculations of acidity constants to be carried out, and, except for solvents with low dielectric constants (14), the relative acidity constants of a series of acids appear to be independent of the base with which the acids are reacted. However, this is not true of the Lewis scheme in any solvent. Lewis himself pointed out that the acidity of an acid would depend upon the particular reference base which is chosen and vice versa (15). Thus, the series of bases Cl^- , Br^- , and I^- , reacting in water with the acid Cd^{2+} , show an increasing order of base strength, whereas with respect to the acid H_3O^+ , the order is inverted. In the same way, CN^- is a very strong base for the acid Ag^+ , but a very weak base for the acid H_3O^+ . Up to the present time little work has been done on the quantitative evaluation of equilibrium constants of nonprotonic acid-base reactions in typical organic solvents. The Lewis scheme is a stimulating one, very helpful in coordinating qualitative observations, and of great usefulness in catalyzed organic reactions. A large number of chemists have elected to continue to treat hydrogen acids as a separate group, and to call the nonprotonic acids Lewis acids. Each concept is quite useful in its own sphere, and there is no reason to force them together in a single category, since this category may be an artificial one.

Neither system provides a theory of acid-base reaction in a detailed mechanistic sense, nor were they intended to do so. They represent, rather, formulations for organizing reactions under one heading which show certain broad common features. The Brønsted scheme in particular is quasi-thermodynamic, and eschews mechanism. It does not matter whether the acid of water has the actual structure H_3O^+ or is H_9O_4^+ , or consists of a series of solvated particles in equilibrium with one another. As long as there is some average number of solvent molecules associated with the proton which does not change markedly with solute concentration, it is possible to measure and to calculate acidity constants for acids in that solvent, and to represent the solvent acid symbolically as H_3O^+ or $\text{C}_2\text{H}_5\text{OH}_2^+$. There is evidence that in aqueous solutions of very high neutral salt content the hydronium ion becomes much more acidic, and may well have fewer waters of hydration (that is, the leveling effect may have been partly reversed) (16). The Brønsted formulation would still refer to the solvent acid as H_3O^+ , but there would be a change in the autoprotolysis constant of the medium. As investigations are continued into the complexities of acid-base reactions in low dielectric constant media, the detailed modes of acid-base interaction will have to be evaluated. Already it is known that ion-pair formation makes the relative order of acidity of acids dependent on the choice of the reference base (14);

that the apparent equilibrium constant is markedly dependent on concentration because of the formation of triple ions, quadrupoles, and higher ionic aggregates (17); that solvents which solvate poorly, like the nitro compounds, may force a change in the stoichiometry of an acid-base reaction as a function of concentration (18); that different aprotic solvents cause shifts in the equilibrium constant of a given acid-base reaction (19); and that an acid indicator may show different colors with different classes of bases (20). Undoubtedly other such complexities will appear in the future. Although the occurrence of these complexities has, in itself, nothing to do with the Brønsted definition, the successful application of the Brønsted scheme to them presents an interesting challenge.

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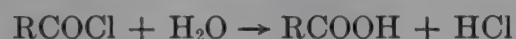
Polytechnic Institute of Brooklyn

ACID HALIDES

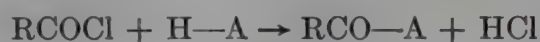
Acid halides are compounds that react with water to yield the parent acids and hydrogen halide, and therefore may be considered a special type of mixed acid anhydride (see Acid anhydrides). Structurally they are derived from acids, either in-

organic or organic, by replacement of one or more hydroxyl groups in the acid function by halogen. Thus, among inorganic compounds, SO_2Cl_2 , sulfuryl chloride, is the full acid chloride of sulfuric acid, considered as $\text{SO}_2(\text{OH})_2$, and ClSO_3H , chlorosulfonic acid, is its half-chloride (see Chlorosulfonic acid; Sulfur compounds). The two most important types of organic acid chlorides (acyl chlorides) are those derived from carboxylic acids, of type formula RCOCl , and those derived from sulfonic acids, of type formula RSO_2Cl , where R is any hydrocarbon radical (see Table 1). Both types are usually named from the corresponding acids, and the most familiar ones are acetyl chloride, CH_3COCl ; oxalyl chloride, $(\text{COCl})_2$; benzoyl chloride, $\text{C}_6\text{H}_5\text{COCl}$; phosgene or carbonyl chloride, COCl_2 ; chloroformic or chlorocarbonic acid, known in the form of its esters, ROCOCl ; and benzenesulfonyl chloride, $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ (see Acetic acid; Benzoic acid; Phosgene; etc). The technological importance of the chlorides is comparatively small, doubtless because the cheaper and less corrosive anhydrides will generally serve as well (see Acid anhydrides).

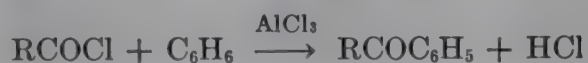
In physical properties the acyl chlorides are typical organic liquids, with irritating odors; phosgene is gaseous, and some of the higher chlorides are solids. The carboxylic acid chlorides boil at lower temperatures than the corresponding acids, and in general without decomposition. They are soluble in such organic solvents as ether and chlorinated hydrocarbons. Chemically they are quite reactive, fuming in air and corroding metals in the presence of moisture because of the acids liberated.



In general, acyl chlorides combine with any compound ($\text{H}-\text{A}$ in the equation below) containing a hydrogen atom linked to oxygen, sulfur, or nitrogen; the reaction is called acylation (see Esterification).



Carboxylic acid chlorides are usually more reactive than sulfonic acid chlorides; aliphatic carboxylic acid chlorides are more reactive than aromatic acid chlorides. Acyl chlorides convert alcohols to esters, and ammonia and amines to amides. Even hydrogen on a benzene ring can be replaced (see Friedel-Crafts reaction).



Their reduction to aldehydes (Rosenmund reaction) is of laboratory interest only.

The organic acid chlorides find some use as intermediates in the manufacture of dyes (phosgene) and pharmaceuticals, particularly the sulfa drugs (*p*-acetamido-benzenesulfonyl chloride). In the laboratory they are valuable tools in synthesis, in detecting the presence of hydroxyl groups in organic molecules, and otherwise in identifying organic compounds (as in the Hinsberg test for distinguishing between primary and secondary amines by means of sulfonyl chlorides).

Carboxylic acid chlorides are usually prepared directly from the corresponding acids or sodium salts, by the use of any of a variety of inorganic reagents, such as phosphorus halides and thionyl or sulfuryl chloride.



Thionyl chloride has the advantage that only gaseous by-products are formed. Phosphorus oxychloride, POCl_3 , may be used with salts. Benzoyl chloride is manufactured by chlorination of benzaldehyde at the aldehyde group,



This mode of synthesis is applicable only to aldehydes which bear no hydrogen atoms at the α -carbon atom. Phosgene, COCl_2 , is prepared by chlorination of carbon monoxide.

Sulfonyl chlorides are available from the corresponding sulfonic acids or their salts by the same methods as those used in preparing carboxylic acid chlorides. In addition, they may also be prepared from aromatic hydrocarbons by direct chlorosulfonation with chlorosulfonic acid, an excess of reagent being used in this reaction.

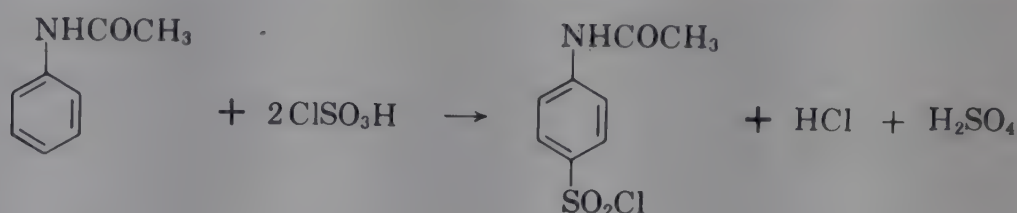


Table 1. Important Organic Acid Halides

Name	Formula	Mp, °C	Bp, °C	d_4^{20}
acetyl fluoride	CH_3COF	< -60	20.5	0.993
acetyl chloride	CH_3COCl	-112	51–52	1.1051
acetyl bromide	CH_3COBr	-96.5	76.7	1.663_4^{16}
acetyl iodide	CH_3COI		104–106	2.067
propionyl chloride	$\text{CH}_3\text{CH}_2\text{COCl}$	-94	80	1.065
butyryl chloride	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COCl}$	-89.0	102 (99–102)	1.028
chloroacetyl chloride	ClCH_2COCl		108–110 (105–106)	1.495_4^0
benzoyl chloride	$\text{C}_6\text{H}_5\text{COCl}$	-1	197 (194 ⁷⁴²)	1.2187_{18}^{15}
phosgene (carbonyl chloride)	COCl_2	$-118 (-104)$	8.3	1.392_4^{19}
ethyl chloroformate (chlorocarbonate)	$\text{C}_2\text{H}_5\text{OCOCl}$	-80.6	94	1.138
benzenesulfonyl chloride	$\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$	14.5 (fp, 0)	246–247 dec	1.378 ²³
1-naphthalenesulfonyl chloride	$\text{C}_{10}\text{H}_7\text{SO}_2\text{Cl}$	68	195 ¹³	
2-naphthalenesulfonyl chloride	$\text{C}_{10}\text{H}_7\text{SO}_2\text{Cl}$	76	201 ¹³	
<i>p</i> -toluenesulfonyl chloride	$\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{Cl}$	69	146 ¹⁵	

NOTE: Specific gravity is indicated as d_4^{20} unless otherwise shown.

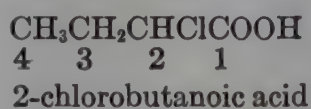
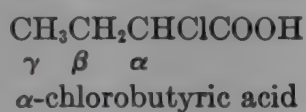
“Acid halides” in *ECT* 1st ed., Vol. 1, pp. 138–139, by O. C. Dermer, Oklahoma Agricultural and Mechanical College.

ACIDS, CARBOXYLIC

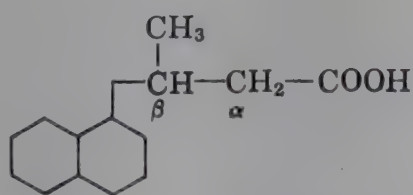
Carboxylic acids are characterized by the presence of one or more carboxyl groups, $\begin{array}{c} \text{O} \\ \parallel \\ \text{—C—OH} \end{array}$ (usually written —COOH). The hydrogen atom of this group is active and may appear as an ion, thus justifying the name acid. Organic carboxylic acids, RC—OOH , may be classified as aliphatic, alicyclic, aromatic, and heterocyclic; as saturated and unsaturated; as unsubstituted and substituted; as monocarboxylic, dicarboxylic, etc. Carbonic acid, HOCOOH ; chloroformic or chlorocarbonic acid, ClCOOH ; and carbamic acid, NH_2COOH , are not always included among organic carboxylic acids. (For the esters of these acids, see Carbonic and chloroformic esters, and Urethans, respectively; see also Amino acids.)

Nomenclature

There are three principal methods of naming carboxylic acids: (1) by common names, usually ending in “-ic” and based on either observed sources in nature (as acetic acid, from the Latin *acetum*, vinegar; benzoic acid, from benzoin) or on the compounds from which the carboxylic acids are derived (naphthoic acid, from naphthalene; nicotinic acid, from nicotine); (2) by the Geneva system, modified by the IUPAC, in which the ending “-oic” or “-dioic” (acid) is added to the name of the related hydrocarbon that has the same number of carbon atoms as the acid (acetic acid, CH_3COOH , is thus named ethanoic acid from ethane, CH_3CH_3 ; and $\text{HOOC}(\text{CH}_2)_4\text{CH}:\text{CHCOOH}$, 2-octenedioic acid); and (3) by the “-carboxylic” nomenclature (also approved by the IUPAC), in which “-carboxylic acid” is added to the name of the hydrocarbon from which the acid is considered to be derived by the substitution of COOH for hydrogen (acetic acid would then be methanecarboxylic acid, and 1-naphthoic acid would be 1-naphthalenecarboxylic acid). The Geneva system is used only for aliphatic acids, usually only mono- and dicarboxylic acids. Carboxylic acid names may be used for cyclic compounds (alicyclic, aromatic, or heterocyclic) in which the carboxyl group is attached directly to the ring, or for aliphatic polycarboxylic acids. For acids in which the carboxyl group is attached to a side chain, “additive names,” such as 1-naphthaleneacetic acid (a synonym of 1-naphthylacetic acid) for $\text{C}_{10}\text{H}_7\text{CH}_2\text{COOH}$, are very convenient. For designating the positions of substituents, Greek letters are used with the common names, numerals with the IUPAC names.



It should be noted that the Greek letters start with the carbon next to the carboxyl, whereas the numerals count the carboxyl carbon as 1; thus α corresponds to 2, β to 3, etc. In additive names the Greek letters are often used to simplify nomenclature, as in



β -methyl- β -naphthalenepropionic acid (preferred), or
3(1-naphthyl)butanoic acid.

For other examples, see Tables 2 to 10.

General Properties

Although organic acids, as a group, are usually considered to be relatively weak acids, most carboxylic acids are stronger than the weakest of the inorganic acids. Furthermore, the introduction of negative substituents and of additional carboxyl groups into organic acids increases the strength of these acids if the substituent groups are sufficiently close to the carboxyl group; thus, while the ionization constants, K , for unsubstituted saturated aliphatic monocarboxylic acids (except formic acid) vary little among themselves, the introduction of successive chlorine atoms may lead to a progressive increase in the ionization constants, so that trichloroacetic acid, for ex-

ample, approaches the strong mineral acids in strength. The most influential positions for substituents are the α -position in aliphatic acids and the *o*-position in aromatic acids. Ionization constants of representative carboxylic acids are given in Table 1.

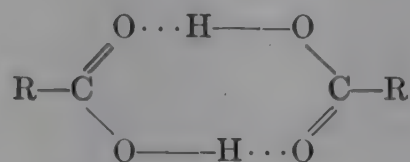
Table 1. Dissociation Constants of Carboxylic Acids in Aqueous Solutions

Monocarboxylic acids					
Acids	<i>K</i>	°C ^a	Acids	<i>K</i>	°C ^a
<i>Aliphatic</i>			<i>Aromatic</i>		
<i>Unsubstituted</i>			<i>Unsubstituted</i>		
formic	1.77×10^{-4}	20	benzoic	6.46×10^{-5}	20
acetic	1.76×10^{-5}		<i>o</i> -toluic	1.22×10^{-4}	
propionic	1.34×10^{-5}		<i>m</i> -toluic	5.2×10^{-5}	
butyric	1.54×10^{-5}	20	<i>p</i> -toluic	4.33×10^{-5}	
isobutyric	1.44×10^{-5}	18	α -naphthoic	2×10^{-4}	
<i>trans</i> -crotonic	2.03×10^{-5}		β -naphthoic	6.8×10^{-5}	
<i>Substituted</i>			phenylacetic	5.2×10^{-5}	18
chloroacetic	1.40×10^{-3}		<i>trans</i> -cinnamic	3.65×10^{-5}	
dichloroacetic	3.32×10^{-2}		<i>Substituted</i>		
trichloroacetic	2×10^{-1}		<i>o</i> -chlorobenzoic	1.20×10^{-3}	
bromoacetic	2.05×10^{-3}		<i>m</i> -chlorobenzoic	1.51×10^{-4}	
iodoacetic	7.5×10^{-4}		<i>p</i> -chlorobenzoic	1.04×10^{-4}	
glycolic	1.48×10^{-4}		<i>o</i> -nitrobenzoic	6.95×10^{-3}	18
cyanoacetic	3.65×10^{-3}		<i>m</i> -nitrobenzoic	3.4×10^{-4}	
α -chloropropionic	1.47×10^{-3}		<i>p</i> -nitrobenzoic	3.93×10^{-4}	
β -chloropropionic	1.04×10^{-4}		<i>m</i> -hydroxybenzoic	8.7×10^{-5}	19
lactic	8.4×10^{-4}	100	<i>p</i> -hydroxybenzoic	3.3×10^{-5}	19
<i>Alicyclic</i>			anisic	3.38×10^{-5}	
cyclohexanecarboxylic			gallic	3.9×10^{-5}	
(hexahydrobenzoic)	1.26×10^{-5}		<i>m</i> -aminobenzoic	1.67×10^{-5}	
<i>Heterocyclic</i>			<i>p</i> -aminobenzoic	1.2×10^{-5}	
furoic	6.76×10^{-4}				
2-thiophenecarboxylic	3.3×10^{-4}				
Di- and tricarboxylic acids					
Acids	<i>K</i> (1st H)		<i>K</i> (2nd H)	<i>K</i> (3rd H)	°C ^a
<i>Aliphatic</i>					
oxalic	5.90×10^{-2}		6.40×10^{-5}		
malonic	1.49×10^{-3}		2.03×10^{-6}		
succinic	6.89×10^{-5}		2.47×10^{-6}		
adipic	3.71×10^{-5}		3.87×10^{-5}		18
<i>trans</i> -fumaric	9.30×10^{-4}		3.62×10^{-5}		18
maleic	1.42×10^{-2}		8.57×10^{-7}		
malic	3.9×10^{-4}		7.8×10^{-6}		
α -tartaric	1.04×10^{-3}		4.55×10^{-5}		
citric	8.4×10^{-4}		1.8×10^{-5}	4.0×10^{-6}	18
<i>Aromatic</i>					
<i>o</i> -phthalic	1.3×10^{-3}		3.9×10^{-5}		
<i>o</i> -phenylenediacetic	1.1×10^{-4}				

^a Temperature is 25°C unless otherwise stated.

The association of carboxylic acids was first observed by determining vapor densities of the acids and freezing or boiling points of acid solutions in certain solvents.

Two molecules of a monobasic acid are now considered to be associated by means of hydrogen bonds,



This assumption is confirmed by electron-diffraction measurements. In the presence of foreign molecules, as of solvents which form hydrogen bonds either as donors or as acceptors of hydrogen, the association of the acids diminishes accordingly. The hydrogen bonds formed with the foreign molecules replace the bonds that are responsible for the association. Thus, there is less association of carboxylic acids in water, alcohol, ketones, and similar solvents than there is in aprotic solvents, like benzene and carbon tetrachloride. Acetic acid in benzene is almost completely associated to the dimer. Esters of carboxylic acids, on the other hand, are not associated.

Carboxylic acids, as typical acids, form metal salts, RCOOM , which are all solids; the sodium and potassium salts are, in general, more soluble in water and less soluble in organic solvents than are the corresponding acids. Metal salts of long-chain acids (C_{11} to C_{18}) form colloidal solutions in water and appear in commerce as soaps (see Driers and metallic soaps). Carboxylic acids also form esters, RCOOR' , more or less readily by acid-catalyzed esterification (see Esterification; Esters, organic). On dehydration, carboxylic acids yield anhydrides, $(\text{RCO})_2\text{O}$ (see Acid anhydrides). Dicarboxylic acids may form either normal ("neutral") or "acid" salts or esters. Sodium succinate, $\text{NaOOC}(\text{CH}_2)_2\text{COONa}$, and sodium hydrogen succinate, $\text{HOOC}(\text{CH}_2)_2\text{COONa}$, illustrate a salt and an "acid" salt; methyl oxalate, $\text{H}_3\text{COOC}.\text{COOCH}_3$, and methyl hydrogen oxalate, $\text{HOOC}.\text{COOCH}_3$, illustrate an oxalic ester and an oxalic "acid" ester. Other derivatives characterized by the RCO (acyl) group and obtainable by replacement of the hydroxyl group instead of the acidic hydrogen are acid halides (qv), RCOX , and amides (qv), RCONH_2 . Nitriles (qv), $\text{RC}:\text{N}$, are regarded as carboxylic acid derivatives because they can be obtained by the dehydration of ammonium salts or amides of the acids and because they yield the acids on hydrolysis. Ketenes (qv), $\text{RCH}:\text{CO}$ and $\text{RR}'\text{C}:\text{CO}$, may be considered internal anhydrides of carboxylic acids; they can be prepared indirectly from the acids and can, in turn, be hydrolyzed to the acids.

The fully hydrated forms (*ortho acids*), $\text{RC}(\text{OH})_3$, of carboxylic acids are known in the form of their esters, such as ethyl orthoformate, $\text{HC}(\text{OC}_2\text{H}_5)_3$. *Per acids* (more systematically called *peroxy acids*) may be represented by the general formula $\text{RCO}(\text{O}_2)\text{H}$, such as perbenzoic acid, $\text{C}_6\text{H}_5\text{CO}(\text{O}_2)\text{H}$, and *acyl peroxides* by $(\text{RCO})_2\text{O}_2$, such as benzoyl peroxide $(\text{C}_6\text{H}_5\text{CO})_2\text{O}_2$. In *thio acids* (qv), either one or both of the oxygen atoms of the carboxyl group may be replaced by sulfur, as in dithioacetic acid, $\text{CH}_3\text{-CSSH}$.

It is sometimes desirable to decarboxylate carboxylic acids. A loss of carbon dioxide is produced with relative ease, depending upon the nature of the acid as in $\text{RCOOH} \rightarrow \text{RH} + \text{CO}_2$. Some acids decarboxylate quite easily, as by moderate heating (acetoacetic, nitroacetic, and malonic acids); others require more drastic conditions, such as fusion of the sodium salt with alkali (eg, sodium acetate to give methane) or heating to sufficiently high temperatures (eg, furoic acid above 200°C , in the presence of a copper catalyst if desired, to give furan).

Carboxylic acids may be characterized by the preparation of their anilides, *p*-toluidides or phenacyl ($\text{C}_6\text{H}_5\text{COCH}_2-$), *p*-bromophenacyl, or other solid substituted phenacyl esters.

Aliphatic Acids

Physical and Chemical Properties. (See Tables 2 to 6.) The monocarboxylic acids of low carbon content (C_1 – C_4 , with straight chains) are corrosive liquids of pungent or offensive odor, and are miscible with water. Those of next-higher carbon content (C_5 – C_9) are oily liquids, sparingly soluble in water, with an unpleasant odor. The members of the series from C_{10} upward are water-insoluble solids. The di- and polycarboxylic acids are all solid crystalline compounds; the simpler ones have moderate to high solubilities in water. The physical constants of the substituted acids, like their acid strengths, are functions of the nature, number, and position of their substituents.

In addition to the reactions characteristic of all carboxylic acids, the aliphatic acids react with chlorine or bromine in the presence of sunlight or certain catalysts, such as iodine, to form halogen-substituted acids. If a small amount of phosphorus trihalide is used as catalyst, substitution occurs at the α -position. The chemical properties of substituted carboxylic acids vary with the nature and the positions of the substituents. For example, when halogen-substituted acids are heated with alkali, the α -substituted acids exchange the halogen for a hydroxyl group; the β -acids lose hydrogen halide and yield the unsaturated acids; and the γ -acids form lactones (intramolecular esters). Hydroxy acids lose water to produce three types of products: the α -hydroxy acids give lactides (cyclic double esters) by the interaction of two molecules of acid under the influence of heat; the β -hydroxy acids, when heated, form unsaturated acids; whereas the γ - and δ -acids readily form lactones, even at ordinary temperatures. The aldehydo and keto acids exhibit chemical characteristics of both the carbonyl group (see Aldehydes; Ketones) and the carboxyl group.

Occurrence. The monocarboxylic acids are widely distributed in nature. The lower acids (C_1 – C_5) are found in many plant and animal liquids such as plant saps, perspiration, and urine. The intermediate and higher acids containing an even number of carbon atoms occur in a wide variety of fats (qv), oils, and waxes (qv) in the form of esters (see also Fatty acids); the esters of fats and oils are glycerides, whereas the esters of waxes are derived from higher even-numbered aliphatic alcohols (C_{16} – C_{36}) or from sterols (qv). It is significant from the point of view of their biochemical formation that almost all of the naturally occurring aliphatic acids contain an even number of carbon atoms. A few of the dicarboxylic acids occur naturally, for the most part in plants (see Acids, dicarboxylic). Of the substituted acids that occur in nature or are formed as intermediate products in biochemical processes the most important are the hydroxy acids: lactic, β -hydroxybutyric, ricinoleic, malic, tartaric, and citric; the aldehydo acid: glyoxylic; the keto acids: pyruvic and acetoacetic; and α -amino acids (see Amino acids).

Preparation. In addition to the industrial production of the lower aliphatic acids by fermentation and special procedures (see Formic acid; Ethanoic acid; Propionic acid; Butyric acid) and of the higher fat-forming acids by saponification of naturally occurring glycerides (see Fats and fatty oils; Fatty acids), a number of general pro-

Table 2. Aliphatic Acids: Lower Monocarboxylic (C₁-C₄)

Common name	Synonyms	Formula	Mp, °C	Bp, °C	d ₄ ²⁰	n _D ²⁰
<i>Saturated</i>						
formic	methanoic	HCOOH	8.40	100.7	1.220	1.37137
acetic	ethanoic	CH ₃ COOH	16.6	118.1	1.049	1.37182
propionic	propanoic	CH ₃ CH ₂ COOH	-22	141.1	0.992	1.38736 ^{19.9}
butyric	butanoic	CH ₃ CH ₂ CH ₂ COOH	-7.9	163.5 ⁷⁵⁷	0.9587	1.39906
isobutyric	2-methylpropanoic; α-methylpropionic	(CH ₃) ₂ CHCOOH	-47.0	154.4	0.949	1.39300
<i>Unsaturated</i>						
acrylic	propenoic	CH ₂ :CHCOOH	12.3	141.9	1.062 ¹⁸	1.4224
methacrylic	2-methylpropenoic; α-methylacrylic	CH ₂ :C(CH ₃)COOH	16	163	1.015	1.43143
crotonic (α-, ordinary or solid)	<i>trans</i> (?)-2-butenic; <i>trans</i> (?)-β-methylacrylic	CH ₃ CH:CHCOOH	72	189	1.018	1.4228 ^{79.7}
isocrotonic (liquid)	<i>cis</i> (?)-2-butenic; <i>cis</i> (?)-β-methylacrylic	CH ₃ CH:CHCOOH	14-15	171.9 dec	1.0312 ¹⁵	1.4457
propionic	propynoic; propargylic	CH:CCOOH	9	144 dec	1.139 ¹⁵	

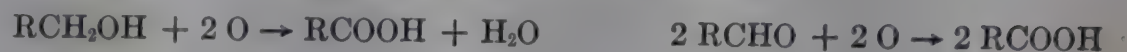
NOTE: Boiling point, bp, is given at 760 mm unless otherwise indicated. Specific gravity is given as d₄²⁰ unless otherwise indicated. Refractive index, n, is likewise given at 20°C unless otherwise shown.

Table 3. Aliphatic Acids: Intermediate Monocarboxylic (C₅-C₁₁)

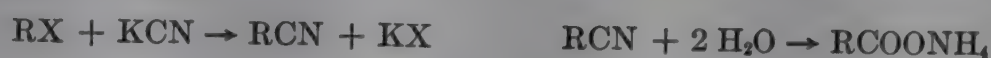
Common name	Synonyms	Formula	Mp, °C	Bp, °C	d ₄ ²⁰	n _D ²⁰
<i>Saturated</i>						
valeric	pentanoic	CH ₃ (CH ₂) ₃ COOH	-34.5	187	0.942	1.4086
isovaleric	3-methylbutanoic	(CH ₃) ₂ CHCH ₂ COOH	-37.6	176.7	0.937 ¹⁵	1.40178 ^{22.4}
caproic	hexanoic	CH ₃ (CH ₂) ₄ COOH	-1.5 to -2.0	205 (202)	0.929	1.41635
enanthic	heptanoic	CH ₃ (CH ₂) ₅ COOH	(-9.5) -10	223.5 (108-110°)	0.9127 ²⁵	1.42162 ^{19.8}
caprylic	octanoic	CH ₃ (CH ₂) ₆ COOH	16	237.5	0.910	1.4285
pelargonic	nonanoic	CH ₃ (CH ₂) ₇ COOH	12	254	0.9055	1.4330
capric	decanoic	CH ₃ (CH ₂) ₈ COOH	31.5	268-270	0.8858 ⁴⁰	1.42855 ⁴⁰
<i>n</i> -undecylic	undecanoic; hendecanoic	CH ₃ (CH ₂) ₉ COOH	29.3	228 ¹⁶⁰	0.8905	1.4294 ^{45.2}
<i>Unsaturated</i>						
sorbic	2,4-hexadienoic	CH ₃ CH:CHCH:CHCOOH	134.5	228 dec		

cedures are available for the synthesis of the carboxylic acids. A few such procedures are as follows:

- (1) Oxidation of primary alcohols or aldehydes.



- (2) Hydrolysis of nitriles (qv), which in turn are usually prepared from alkyl halides. Strong acid is usually employed as catalyst for the hydrolysis, but a basic catalyst may also be used.

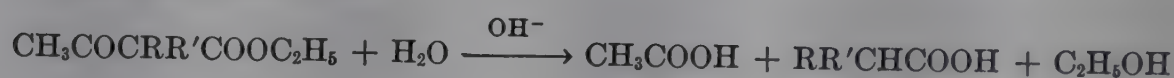
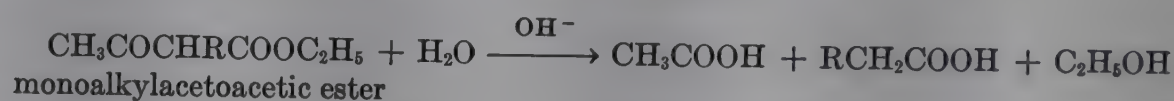


- (3) Hydrolysis of esters, amides, acid chlorides, and acid anhydrides. However, except for the saponification of glycerides, this method is of limited importance since these compounds are generally prepared from the acids.

- (4) Reaction of Grignard reagents with carbon dioxide.

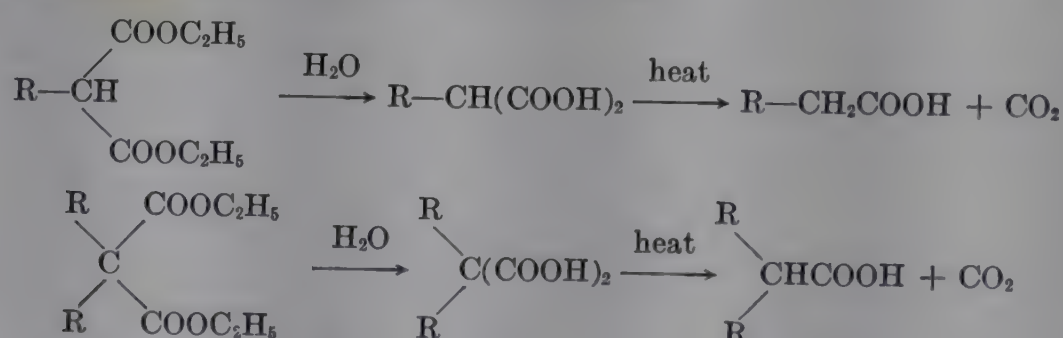


- (5) Acetoacetic ester synthesis. Hydrolysis of alkyl-substituted acetoacetic esters with strong alkali results in the formation of salts of acetic acid and of an alkyl-substituted acetic acid. This hydrolysis is referred to as "acid hydrolysis" ("ketonic hydrolysis," with dilute alkali, gives ketones (qv)).



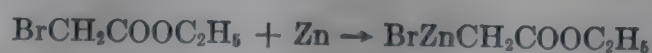
(Alkylated acetoacetic esters are produced by the action of alkyl halides on the sodium derivatives of ethyl acetoacetate.)

- (6) Malonic ester synthesis. Hydrolysis of alkyl-substituted malonic esters (usually the ethyl or methyl esters) yields dicarboxylic acids, which on heating decompose to alkyl-substituted acetic acids and carbon dioxide.



(Alkyl-substituted malonic esters are prepared from alkyl halides and the sodium derivatives of ethyl malonate.)

- (7) Reformatsky reaction. β -Hydroxy acids (and from them, by dehydration, α,β -unsaturated acids) may be prepared in the form of esters from α -halo esters by reaction with an aldehyde or ketone and zinc in anhydrous ether or ether-benzene, followed by hydrolysis.



(R_2 = any two hydrocarbon radicals or a hydrocarbon radical and hydrogen.)

Table 4. Aliphatic Acids: Higher Monocarboxylic (C₁₂-C₃₀)

Common name	Synonyms	Formula	Mp, °C	Bp, °C	d ₄ ²⁰	n _D ²⁰
<i>Saturated</i>						
lauric	dodecanoic	CH ₃ (CH ₂) ₁₀ COOH	44 (48)	225 ₁₀₀	0.8679 ₄ ⁵⁰	1.4183 ^{82.1}
myristic	tetradecanoic	CH ₃ (CH ₂) ₁₂ COOH	58	250.5 ₁₀₀	0.858 ⁶⁰	1.4308 ⁶⁰
palmitic	hexadecanoic	CH ₃ (CH ₂) ₁₄ COOH	64	339-356 dec	0.853 ⁶² (liq)	1.4273 ^{79.8}
margaric	heptadecanoic	CH ₃ (CH ₂) ₁₅ COOH	60.66 (58-59)	227 ₁₀₀	0.8578 ⁶⁰	1.4342 ⁶⁰
stearic	octadecanoic	CH ₃ (CH ₂) ₁₆ COOH	69.4	383	0.847 ⁶⁹	1.4299 ^{80.2}
arachidic	eicosanoic; arachic	CH ₃ (CH ₂) ₁₈ COOH	76.3	328	0.824 ¹⁰⁰ ₄	
behenic	docosanoic	CH ₃ (CH ₂) ₂₀ COOH	80.7 (84)	306 ₆₀		
lignoceric	tetracosanoic	CH ₃ (CH ₂) ₂₂ COOH	81		0.8207	
cerotic	hexacosanoic	CH ₃ (CH ₂) ₂₄ COOH	87.7 (80-82)	dec	0.836 ⁷⁹	1.4440 ⁷⁹
melissic	triacontanoic	CH ₃ (CH ₂) ₂₈ COOH	91.9-92.1			
<i>Unsaturated</i>						
oleic	<i>cis</i> -9-octadecenoic	CH ₃ (CH ₂) ₇ CH:CH(CH ₂) ₇ COOH	14	286 ₁₀₀	0.895 ¹⁸	1.463 ^{17.7}
elaidic	<i>trans</i> -9-octadecenoic	CH ₃ (CH ₂) ₇ CH:CH(CH ₂) ₇ COOH	51.5 (44-45)	288 ₁₀₀	0.851 ⁷⁹	
linoleic	9,12-octadecadienoic; linolic	CH ₃ (CH ₂) ₃ (CH ₂ CH:CH) ₂ (CH ₂) ₇ COOH	-11	230 ₁₆	0.9025	
α-eleostearic	<i>cis</i> (?)-9,11,13-octadecatrienoic	CH ₃ (CH ₂) ₃ (CH:CH) ₃ (CH ₂) ₇ COOH	48-49	235 ₁₂ sl dec		
<i>Unsaturated</i>						
β-eleostearic	<i>trans</i> (?)-9,11,13-octadecatrienoic	CH ₃ (CH ₂) ₃ (CH:CH) ₃ (CH ₂) ₇ COOH	72			
α-linolenic	9,12,15-octadecatrienoic	CH ₃ (CH ₂ CH:CH) ₃ (CH ₂) ₇ COOH		230-232 ¹⁷	0.905	
erucic (<i>cis</i>)	<i>cis</i> -13-docosenoic	CH ₃ (CH ₂) ₇ CH:CH(CH ₂) ₁₁ COOH	33.5 (31-32)	281 ₃₀	0.860 ⁵⁵ ₄	

Table 5. Aliphatic Acids: Di- and Tricarboxylic

Common name	Synonyms	Formula	Mp, °C	Bp, °C	d ₄ ²⁰	n _D ²⁰
<i>Saturated</i>						
oxalic	ethanedioic	HOOC.COOH.2H ₂ O	101; 189 anhyd	150 subl	1.653	1.440, 1.475, 1.625
malonic	propanedioic; methanedicarboxylic	HOOC.CH ₂ .COOH	135.6	dec	1.631 ^{1.5} ₄	
succinic	butanedioic; ethanedicarboxylic	HOOC(CH ₂) ₂ .COOH	185 (189–190)	235 dec	1.564 ^{1.5} ₄	1.450, 1.534, 1.610
glutaric	pentanedioic; 1,3-propanedicarboxylic	HOOC(CH ₂) ₃ .COOH	97.5; 95–96	304 dec	1.429 ^{1.5} ₄	1.4188 ^{106.4}
adipic	hexanedioic; 1,4-butanedicarboxylic	HOOC(CH ₂) ₄ .COOH	151–153	265 ₁₀₀	1.366	
pimelic	heptanedioic; 1,5-pentanedicarboxylic	HOOC(CH ₂) ₅ .COOH	103	272 ₁₀₀ subl	1.329 ¹⁵	
suberic	octanedioic; 1,6-hexanedicarboxylic	HOOC(CH ₂) ₆ .COOH	140	279 ₁₀₀		
azelaic	nonanedioic; 1,7-heptanedicarboxylic	HOOC(CH ₂) ₇ .COOH	106.5	360 dec; 226 ₁₀	1.029	1.4303 ^{110.6}
sebacic	decanedioic; 1,8-octanedicarboxylic	HOOC(CH ₂) ₈ .COOH	133	295 ₁₀₀		1.422 ^{122.3}
tricarballic	1,2,3-propanetricarboxylic; <i>sym</i> -propanetricarboxylic	HOOC.CH ₂ CHCH ₂ .COOH COOH	162–163	dec		
<i>Unsaturated</i>						
maleic	<i>cis</i> -butenedioic	HOOC.CH:CH.COOH	130.5	135 dec	1.590	
fumaric	<i>trans</i> -butenedioic	HOOC.CH:CH.COOH	287 (293–295)	290; subl 200	1.635	
itaconic	methylenebutanedioic; methylene-succinic	HOOC.C.CH ₂ .COOH CH ₂	161 dec	dec	1.632	
acetylenedicarboxylic	butynedioic; ethynedicarboxylic	HOOC.C:C.C.COOH	179			
aconitic	1,2,3-propenetricarboxylic	HOOC.CH ₂ C:CH.COOH COOH	188–197.8 (204)			

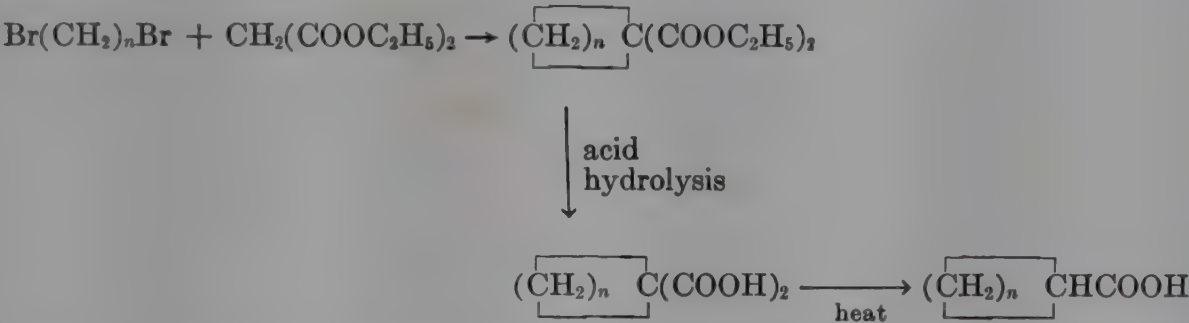
NOTE: If sublimation takes place at a definite temperature, the form subl 200 is used, whereas 200 subl indicates sublimation at 200°C with decomposition.

Alicyclic Acids

This group of acids is characterized by the presence of at least one nonbenzenoid cyclic hydrocarbon skeleton. There may be 3, 4, 5, 6 or more carbon atoms in the ring, and the carboxyl group(s) may be joined directly to the ring or may be separated from it by one or more carbon atoms. (For certain acids, chiefly derivatives of alkylated cyclopentanes and cyclohexanes, occurring in naphthene-base petroleums, see Naphthenic acids; for abietic acid see Rosin; see also Bile constituents.)

Physical and Chemical Properties. (See Table 7.) Purified alicyclic acids are usually crystalline solids with a low water solubility. Their chemical properties are similar to those of the aliphatic carboxylic acids (see Aliphatic acids, page 228). Some of the metallic salts and esters are of considerable industrial importance (see also Alkyd resins).

Preparation. Alicyclic acids are obtained in several ways, some of which involve interesting ring closures. The malonic ester synthesis (see method 6 under Aliphatic acids, page 230) may be adapted for the synthesis of alicyclic acids by the use of polymethylene halides to effect alkylation.



This method, known as the Perkin Ring Closure, can be used to prepare monocarboxylic alicyclic acids having from three to seven members in the ring.

Hydrogenation of aromatic acids is another important source of alicyclic acids.

Aromatic Acids

Aromatic carboxylic acids contain at least one benzene or other aromatic nucleus and one or more carboxyl groups joined directly to the ring or attached to a side chain.

Physical and Chemical Properties. (See Tables 8 and 9.) The aromatic carboxylic acids are crystalline solids, most of them with relatively high melting points. They generally have a rather low water solubility; however, the acids with more than one carboxyl group and a few of the substituted acids show an increased solubility in water. Besides the chemical transformations characteristic of the carboxyl group, the aromatic acids may undergo reactions involving the aromatic nucleus or substituents on the nucleus.

In general, acids that have the carboxyl group separated from the aromatic nucleus (such as phenylacetic and hydrocinnamic) have properties that closely resemble those of the aliphatic carboxylic acids. (See also Tannic acid under Leather and leather processing.)

Occurrence. A few of the most familiar aromatic acids, such as benzoic acid (qv), salicylic acid (qv), gallic acid (qv), and cinnamic acid (qv), occur naturally in free and combined forms in many resins and balsams (see Resins, natural). However, most of the acids are only of synthetic origin.

Table 6. Aliphatic Acids: Substituted

Common name	Synonyms	Formula	Mp, °C	Bp, °C	d ₄ ²⁰	n _D ²⁰
<i>Hydroxy</i> glycolic	hydroxyethanoic; hydroxyacetic; glycollic	CH ₂ OH.COOH	α 63; β 79	dec		
lactic	2-hydroxypropanoic; α- hydroxypropionic	CH ₃ CHOH.COOH				
DL- L(+)-	ordinary lactic sarcosilactic; paralactic; dextrorotatory lactic		18 26	122 ₁₅ dec	1.249 ¹⁵ 1.2485	1.4414
β-hydroxybutyric gluconic	3-hydroxybutanoic <i>gluco</i> -2,3,4,5,6-penta- hydroxyhexanoic	CH ₃ CHOH.CH ₂ COOH CH ₂ OH(CHOH) ₄ COOH	48-50	130 ₁₂		
D-	D- <i>gluco</i> -2,3,4,5,6-penta- hydroxyhexanoic		125-126; (130-132)			
tartronic	2-hydroxypropanedioic; hydroxymalonic	HOOC.CHOH.COOH	158 dec	110-120 subl		
malic	hydroxybutanedioic; hydroxysuccinic	HOOC.CHOH.CH ₂ COOH				
DL- L(-)- tartaric	ordinary malic 2,3-dihydroxybutanedioic; α,β-dihydroxysuccinic	HOOC(CHOH) ₂ COOH.2H ₂ O HOOC(CHOH) ₂ COOH	128.5 100	150 dec 140 dec	1.601 1.595	
DL-	racemic; paratartronic	HOOC(CHOH) ₂ COOH	anhyd at 100; 204- 206		1.697	
L(+)-	ordinary tartaric; dextro- rotatory tartaric	HOOC(CHOH) ₂ COOH	170		1.7598	1.4955, 1.5352, 1.6045
<i>meso</i> - saccharic	<i>gluco</i> - or <i>gulo</i> -2,3,4,5-tetra- hydroxyhexanedioic	HOOC(CHOH) ₄ COOH	anhyd 140		1.666	1.495, 1.536, 1.605
D- <i>gluco</i> -	D- <i>gluco</i> - or L- <i>gulo</i> -2,3,4,5- tetrahydroxyhexanedioic		125-126 dec			
citric	2-hydroxy-1,2,3-propane- tricarboxylic; β- hydroxytricarballic	HOOC.CH ₂ C(OH)(COOH) COOH	- H ₂ O 70-75; 153	dec	1.542 ¹⁵	1.493, 1.498, 1.509 hyd

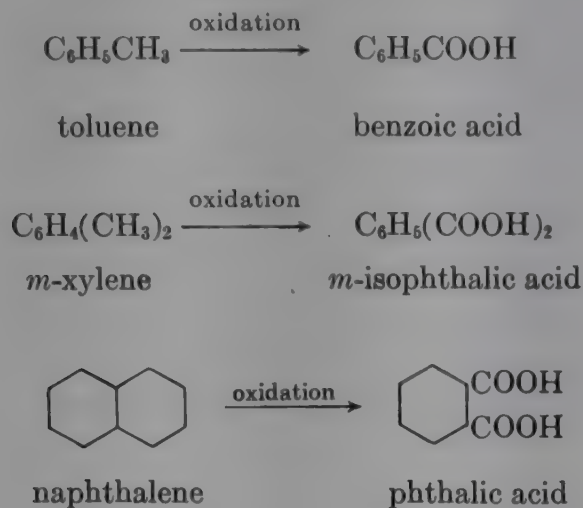
9,10-dihydroxy- stearic	9,10-dihydroxyoctadecan- oic; <i>θ,ε</i> -dihydroxystearic	$\text{CH}_3(\text{CH}_2)_7\text{CHOH}\cdot\text{CHOH}(\text{CH}_2)_7\text{COOH}$	131.5 (136.5)		
ricinoic	12-hydroxy-9-octadecen- oic; ricinoic	$\text{CH}_3(\text{CH}_2)_8\text{CHOH}\cdot\text{CH}_2\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$	γ 5.0 α 7.7 β 16.0	250 ₁₅	0.945 ¹⁶
<i>Aldehydo and Keto</i>					
glyoxylic	oxoethanoic; glyoxalic; oxalaldehydic	O:CH.COOH	dec		
pyruvic	2-oxopropanoic; α -keto- propionic; pyroracemic;	CH ₃ COCOOH	13.6	165 sl dec	1.267
acetoacetic	acetylformic	CH ₃ COCH ₂ COOH		100 dec	
levulinic	3-oxobutanoic; acetyl- acetic	CH ₃ COCH ₂ COOH			
	4-oxopentanoic; γ -keto- valeric	CH ₃ COCH ₂ CH ₂ COOH	37.2	246, 154 ₁₄	1.1395 1.442 ¹⁵³
<i>Halogen-substituted</i>					
chloroacetic	chloroethanoic; mono- chloroacetic; (mono)- chloracetic	ClCH ₂ COOH	α 63 β 55-56 γ 50	189	1.582 ²⁰ 1.4297 ⁶⁵
dichloroacetic	dichloroethanoic; dichloracetic	Cl ₂ CHCOOH	5-6; frz 11	194	1.5634 1.4659 ²²
trichloroacetic	trichloroethanoic; trichloracetic	Cl ₃ CCOOH	57.5	197.5	1.6298 ⁶¹ ₄
bromoacetic	bromoethanoic; mono- bromoacetic; (mono)- bromacetic	BrCH ₂ COOH	50	208	1.934
iodoacetic	iodoethanoic; moniodo- acetic	ICH ₂ COOH	82	dec	
α -chloropropionic	2-chloropropanoic	CH ₃ CHCl.COOH		186	1.28 ⁰ -2.36 ⁹¹⁷ _D
β -chloropropionic	3-chloropropanoic	ClCH ₂ CH ₂ COOH	41 (61)	204	hyg
α -bromobutyric	2-bromobutanoic	CH ₃ CH ₂ CHBr.COOH	-4	212-217 dec; 181-182 ₂₅₀	1.567 ²⁰ ₂
<i>Miscellaneous</i>					
thioglycolic	mercaptoacetic; 2- mercaptoethanoic	HSCH ₂ COOH	-16.5	104-106 ₁₁	1.3253
cynoacetic	cynoethanoic	NCCH ₂ COOH	66 (69-70)	108 ₁₅ , dec 160	

Table 7. Alicyclic Acids

Common name	Synonyms	Formula	Mp, °C	Bp, °C	d_4^{20}	n_D^{20}
cyclopropanecarboxylic	ethyleneacetic	C_3H_5COOH	18-19	182-184 (181)	1.0885	1.43901 ²⁰
cyclopentanecarboxylic	butyleneacetic	C_5H_9COOH	-3	215.5	1.0385 ²⁵	1.4528 ^{17,7}
hydnocarpic	11-(2-cyclopentenyl)hendecanoic	$C_8H_7(CH_2)_{10}COOH$	60.4(+)			
chaulmoogric	13-(2-cyclopentenyl)tridecanoic	$C_8H_7(CH_2)_{12}COOH$				
L(+)-			68.5	247-248 ₂₀		
hexahydrobenzoic	cyclohexanecarboxylic	$C_6H_{11}COOH$	31	233	1.048 ¹⁵ ₄	1.4561 ^{33,6}
2,3,4,5-tetrahydrobenzoic	1-cyclohexene-1-carboxylic	C_6H_9COOH	38	243	1.109	1.4903
abietic	1-4,4a,4b,5,6,10,10a-decahydro-7-isopropyl-1,4a-dimethyl-1-phenanthrenecarboxylic	$C_{19}H_{29}COOH$	172-175			varies with solvent
camphoric	cis-1,2,2-trimethyl-1,3-cyclopentane-dicarboxylic	$C_6H_6(CH_3)_3(COOH)_2$				
DL-			202 (208)			1.228
L(+)-			187			1.186
hexahydrophthalic	1,2-cyclohexanedicarboxylic	$C_6H_{10}(COOH)_2$				
cis-						
trans-						

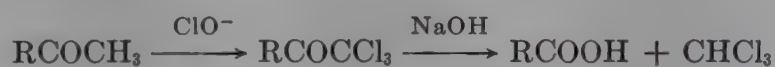
Preparation. In addition to the special industrial procedures for specific aromatic acids (see, eg, Benzoic acid; Phthalic acid), methods similar to those for the synthesis of aliphatic acids are applicable, notably the hydrolysis of nitriles and the Grignard reaction (see Aliphatic acids, page 228). A few other methods, which are of considerable industrial and synthetic importance, are also available.

(1) Oxidation of aromatic hydrocarbons containing side chains or more than one ring results in the formation of aromatic carboxylic acids. For example:



A variety of oxidizing agents have been used industrially, including chlorine, nitric acid, dichromate, and air, in the presence of a catalyst such as vanadium pentoxide. This method is also applicable to substituted hydrocarbons (thus *p*-chlorotoluene may be oxidized to *p*-chlorobenzoic acid).

(2) The oxidation, with hypochlorite, of substituted acetophenones (or acetophenones), RCOCH_3 , is an important method for the preparation of substituted acids.



(R is a substituted aromatic group.) Substituted acetophenones may be prepared by the Friedel-Crafts ketone synthesis. (See also Acetophenone; Friedel-Crafts reaction; Ketones.)

(3) Substitution in the aromatic nucleus serves for the preparation of some substituted acids, but not for the highly substituted, because the carboxyl group attached to an aromatic ring is generally meta-directive and hinders further substitution on the nucleus. Hence the preparation of highly substituted aromatic acids, and also of acids with the carboxyl group attached to side chains, is frequently accomplished by methods specific for the acid in question.

(4) Direct carboxylation of the aromatic nucleus is possible when the ring is sufficiently activated, usually by one or more hydroxyl groups. The process involves treating the alkali metal salt of a phenol with carbon dioxide at an elevated temperature and then acidifying to liberate the hydroxy acid (see Salicylic acid).

Heterocyclic Acids

Heterocyclic acids are characterized by the presence of one or more heterocyclic rings (see Heterocyclic compounds). For a few representative acids see Table 10.

Table 8. Aromatic Acids: Monocarboxylic

Common name	Synonyms	Formula	Mp, °C	Bp, °C	d_4^{20}	n_D^{20}
<i>Carboxyl group attached to ring</i>						
benzoic	benzenecarboxylic	C_6H_5COOH	122	249	1.2659 ₄ ¹⁵	1.53974 ¹⁵
naphthoic		$C_{10}H_7COOH$				
1-	α -naphthoic; 1-naphthalenecarboxylic		160	300		
2-	β -naphthoic; 2-naphthalenecarboxylic		185	300	1.0771 ₄ ⁰	
toluic	methylbenzoic	$CH_3C_6H_4COOH$				
<i>o</i> -			103.7 (104–105)	259.2	1.0621 ₄ ¹⁵	1.512114 ₆ ⁶
<i>m</i> -			108.75 (109–112)	263	1.0541 ₁₂ ²	1.509
<i>p</i> -			179.6	275		
chlorobenzoic		ClC_6H_4COOH				
<i>o</i> -			142	subl	1.544	
<i>m</i> -			158 (154–155)	subl	1.4962 ₅ ⁵	
<i>p</i> -			243 (235)	subl	1.5412 ₄ ⁴	
nitrobenzoic		$NO_2C_6H_4COOH$				
<i>o</i> -			147.5 (144–145)		1.575 ₄ ⁴	
<i>m</i> -			141.4		1.494 ₄ ⁴	
<i>p</i> -			242.4	subl	1.5503 ₂ ²	
3,5-dinitrobenzoic		$(NO_2)_2C_6H_3COOH$	204–205	subl		
salicylic acid		HOC_6H_4COOH	159	subl 76	1.443	1.565
hydroxybenzoic		HOC_6H_4COOH				
<i>m</i> -	<i>o</i> -hydroxybenzoic		201.3 (199–200)		1.473 ₄ ⁴	
<i>p</i> -			213 (214.5–215.5)	subl 76		
gallic	3,4,5-trihydroxybenzoic	$(HO)_3C_6H_2COOH$	220 dec	dec	1.694 ₄ ⁴	
anisic	<i>p</i> -methoxybenzoic; <i>p</i> -anisic	$CH_3OC_6H_4COOH$	184.2	280	1.385 ₄ ⁴	
veratric	3,4-dimethoxybenzoic	$(CH_3O)_2C_6H_3COOH$	anhyd 181	subl		
anthranilic	<i>o</i> -aminobenzoic	$NH_2C_6H_4COOH$	145	subl		
aminobenzoic		$NH_2C_6H_4COOH$				
<i>m</i> -			174 (179.5)	subl	1.511	
<i>p</i> -			187			

Carboxyl group not attached to ring

phenylacetic	α -toluic	$C_6H_5CH_2COOH$	76.7	265.5	1.228
2,4-dichlorophenoxyacetic	2,4-D	$Cl_2C_6H_3OCH_2COOH$	138-140		
hydrocinnamic	β -phenylpropionic	$C_6H_5CH_2CH_2COOH$	48.6	279.8	1.071 ⁴⁹
γ -phenylbutyric	3-phenyl-1-propanecarboxylic	$C_6H_5(CH_2)_3COOH$	51.7	171 ₁₅	
cinnamic (ordinary or trans)	trans- β -phenylacrylic; trans-benzene-propenoic	$C_6H_5CH:CHCOOH$	133	300	1.2475 ⁴
1-naphthaleneacetic	α -naphthylacetic	$C_{10}H_7CH_2COOH$	131		
mandelic	phenylglycolic	$C_6H_5CHOH.COOH$	118.1	dec	1.300; 1.3614
DL-			133		1.341
D(-)-					

Table 9. Aromatic Acids: Di- and Polycarboxylic

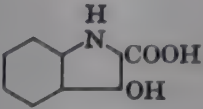
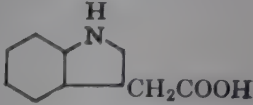
Common name	Synonyms	Formula	Mp, °C	Bp, °C	d ₄ ²⁰	n _D ²⁰
Carboxyl groups attached to ring						
phthalic	1,2-benzenedicarboxylic; o-phthalic	$C_6H_4(COOH)_2$	206-208 dec	dec >191	1.593	
isophthalic	1,3-benzenedicarboxylic; m-phthalic	$C_6H_4(COOH)_2$	345-347	subl		
terephthalic	1,4-benzenedicarboxylic; p-phthalic	$C_6H_4(COOH)_2$	subl	subl ca 300	1.510	
diphenic	2,2'-biphenyldicarboxylic; o,o'-bibenzoic	$HOOC.C_6H_4.C_6H_4.COOH$	228-229	subl		
mellitic	benzenehexacarboxylic	$C_6(COOH)_4$	286	dec		

Carboxyl groups not attached to ring

homophthalic	o-carboxy- α -toluic	$HOOC.C_6H_4CH_2COOH$	175			
o-phenylenediacetic	1,2-benzenediacetic	$C_6H_4(CH_2COOH)_2$	150			

NOTE: If decomposition on heating occurs at a definite temperature, the form dec 191 is used, but if melting or boiling, accompanied by decomposition, sets in at 191 °C, then 191 dec is used.

Table 10. Heterocyclic Acids

Common name	Synonyms	Formula	Mp, °C	Bp, °C
picolinic acid	2-pyridinecarboxylic	C ₅ H ₄ NCOOH	137	subl
nicotinic	3-pyridinecarboxylic	C ₅ H ₄ NCOOH	234–237	subl
indoxylic	3-hydroxy-2-indolecarboxylic; indogenic			subl 123
3-indoleacetic	heteroauxin; β-indolylacetic		165	
cinchoninic	4-quinolinecarboxylic; cinchonic	C ₉ H ₆ NCOOH	253–254	
furoic	2-furancarboxylic; 2-furoic; pyromucic	C ₄ H ₃ OCOOH	133	230–233
2-thiophenecarboxylic	α-thiophenic	C ₄ H ₃ SCOOH	126.5	260 dec
quinolinic	2,3-pyridinedicarboxylic	C ₆ H ₃ N(COOH) ₂	190 dec (195)	
acridinic	2,3-quinolinedicarboxylic	C ₉ H ₅ N(COOH) ₂	105 dec	

“Acids, Carboxylic” in *ECT* 1st ed., Vol. 1, pp. 139–151, by E. F. Landau, Celanese Corporation of America.

ACIDS, DICARBOXYLIC

The acids covered here by the term dicarboxylic are those compounds with two carboxyl groups in the saturated aliphatic series, the first member of which is oxalic acid. The general formula for the group is HOOC(CH₂)_{*n*}COOH. In the best-known members of the group the value of *n* ranges from 0 to around 12; higher members of the series are known, but they have not shown the industrial importance of lower members. For the first five acids in this class, see Oxalic acid, Malonic acid, Succinic acid, Glutaric acid, and Adipic acid. (See also Acids, carboxylic.) Aromatic dibasic acids are not discussed here; see Phthalic acids. Physical properties for those acids for which *n* = 0 to 8 (oxalic through sebacic) are given on p. 232. Physical properties for higher members of the series are given in references 1 through 5. The first fourteen acids in the series and their formulas are given in Table 1.

Table 1. Dicarboxylic Acids

Name	Formula	Value of <i>n</i>	Name	Formula	Value of <i>n</i>
oxalic	HOCCOOH	0	azelaic	HOOC(CH ₂) ₇ COOH	7
malonic	HOOCCH ₂ COOH	1	sebacic	HOOC(CH ₂) ₈ COOH	8
succinic	HOOC(CH ₂) ₂ COOH	2	undecanedioic	HOOC(CH ₂) ₉ COOH	9
glutaric	HOOC(CH ₂) ₃ COOH	3	dodecanedioic	HOOC(CH ₂) ₁₀ COOH	10
adipic	HOOC(CH ₂) ₄ COOH	4	tridecanedioic	HOOC(CH ₂) ₁₁ COOH	11
pimelic	HOOC(CH ₂) ₅ COOH	5	tetradecanedioic	HOOC(CH ₂) ₁₂ COOH	12
suberic	HOOC(CH ₂) ₆ COOH	6	pentadecanedioic	HOOC(CH ₂) ₁₃ COOH	13

Nomenclature. The aliphatic dicarboxylic acids, HOOC(CH₂)_{*n*}COOH, are best known by trivial names for *n* up to 8, as shown in Table 1 above. IUPAC names are

given in Table 1 for higher acids. Thus, the acid



with a total of twelve carbon atoms (10 CH₂'s) is *dodecanedioic acid* (dodecane = 12); it can also be referred to as *1,10-decanedicarboxylic acid*.

To identify substituents, numbers are used as shown in the IUPAC system. Greek letters can also be used, but it must be noted that α corresponds to 2, β to 3.

All the acids are well-defined colorless crystalline solids. An interesting fluctuation has been observed in the physical properties of neighboring members of the series—for example, glutaric acid with five carbon atoms melts at 97.5°C whereas succinic acid with four carbons melts at 186°C. The contrast becomes less marked in acids with higher molecular weights, as shown by Figure 1.

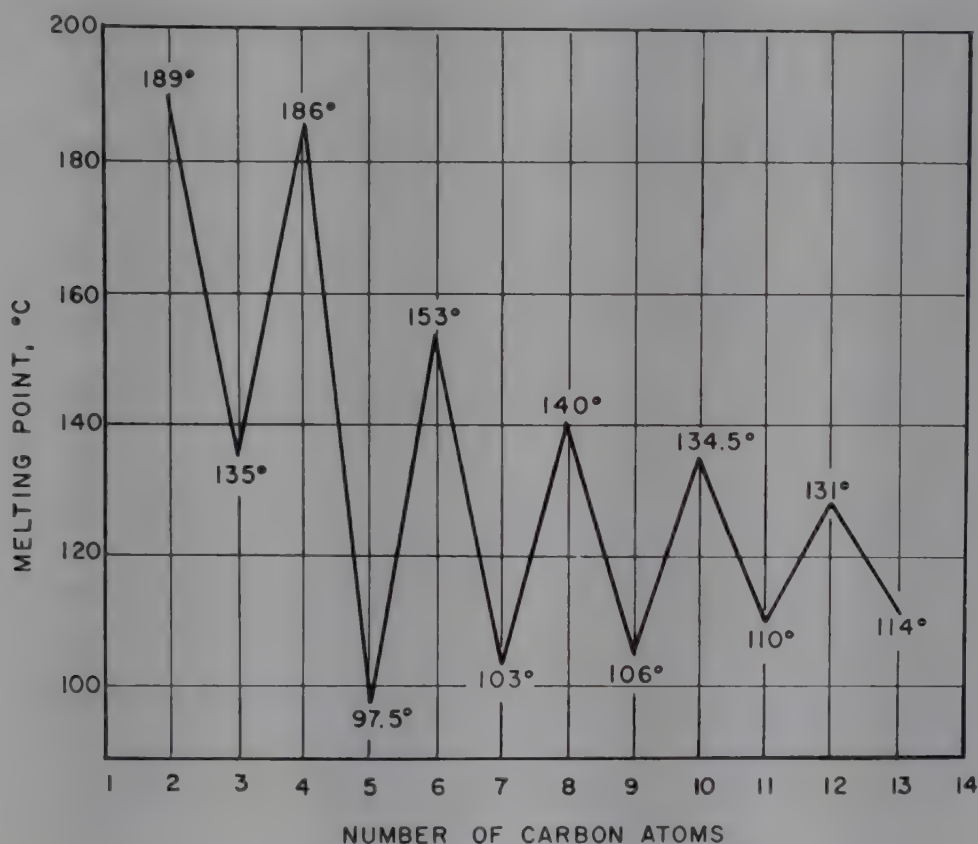


Fig. 1. Melting points of straight-chain dicarboxylic acids.

Lower-molecular-weight acids are water soluble, giving an acidic reaction, and the water solubilities of the odd members are higher than those of the preceding even acids. This is shown in Figure 2.

This alternating relationship does not extend to the boiling points of the acids which rise with increasing molecular weight as shown in Figure 3.

The alternating variation between adjacent odd and even acids has been demonstrated in the ease of decarboxylation of these acids as shown in Table 2 where the decarboxylation temperature is the lowest temperature at which CO₂ is evolved.

The even acids are more difficult to decompose than the odd ones preceding them. The activation energy of this reaction for higher members of the series is fairly high, on the order of 60 kcal/mole for adipic acid whereas malonic acid has an activation energy of decarboxylation of approximately 30 kcal/mole. An investigation has been

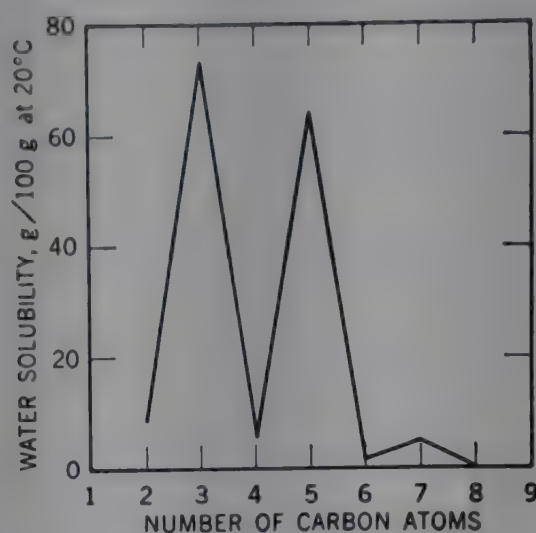


Fig. 2. Water solubilities of straight-chain dicarboxylic acids.

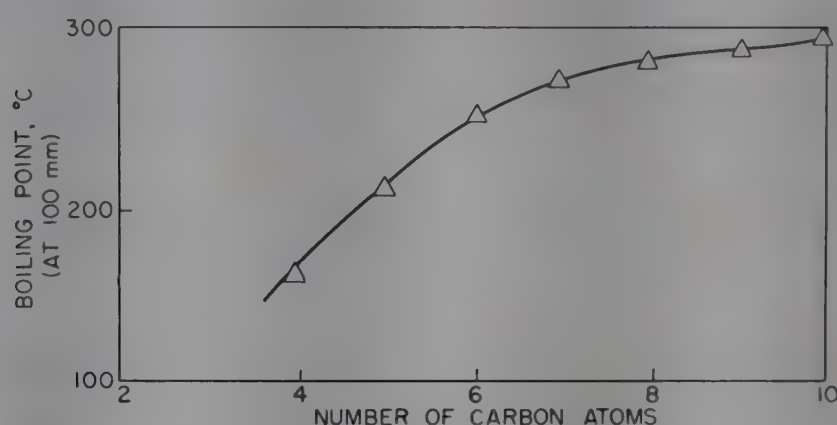


Fig. 3. Boiling points of straight-chain dicarboxylic acids.

carried out to explain the alternation in the properties of the acids, using x-ray crystallographic studies (7). It was found that the even acids have the two carboxyl groups in the molecule in a parallel position, but in the odd acids, the two carboxyls are positioned spatially at 60° . Energetic considerations show that the carbon chain in the even acids is free to position itself more easily with respect to the carboxyl groups, whereas the odd acid chain requires a twisted configuration for packing its angled carboxyls into the crystal lattice. The twisted configuration increases the energy level

Table 2. Decarboxylation Temperatures (6)

Acid	Decarboxylation temp, °C	Acid	Decarboxylation temp, °C
oxalic	170	pimelic	
malonic	150	suberic	350
succinic	300	azelaic	330
glutaric	285	sebacic	360
adipic	310		

about 2 kcal/mole above that of the same molecule in a plane configuration. This increased energy requirement has been proposed as the reason for the alternate fluctuations in melting points and water solubilities.

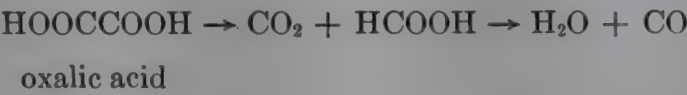
Another property of the acids which does not show the "hunting" effect is the molar heat of combustion; like the boiling point it rises steadily with increasing molecular weight.

Table 3. Molar Heats of Combustion

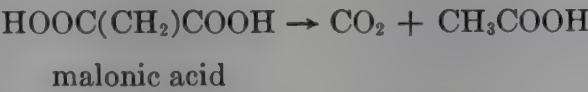
Acid	Molar heat of combustion, kcal/g molecular wt	Acid	Molar heat of combustion, kcal/g molecular wt
oxalic	60.2	pimelic	
malonic	207.2	suberic	985.2
succinic	357.1	azelaic	1141.7
glutaric	514.9	sebacic	1297.3
adipic	669.0		

Chemical Reactions

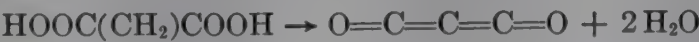
The chemical reactions of the dicarboxylic acids depend mainly on the terminal carboxyls with their reactive hydroxyl groups. Heat-induced chemical decomposition of the acids results either in decarboxylation to a monocarboxylic acid or in anhydride formation with water elimination. Oxalic acid gives carbon dioxide and formic acid, which may itself decompose further.



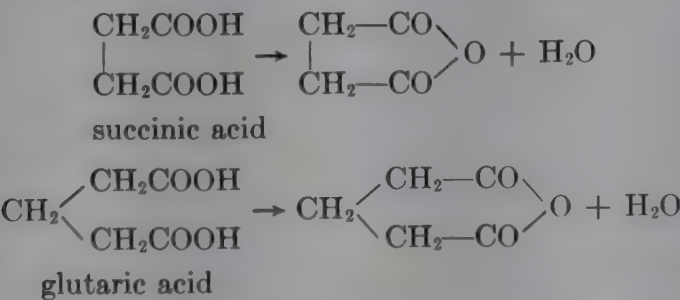
The dibasic acids undergo all the reactions of the monocarboxylic acids (see also Acids, carboxylic) with some interaction peculiar to the presence of two carboxyl groups in proximity. This is demonstrated by the facile elimination of carbon dioxide from malonic acid where the carboxyls are both attached to the same carbon.



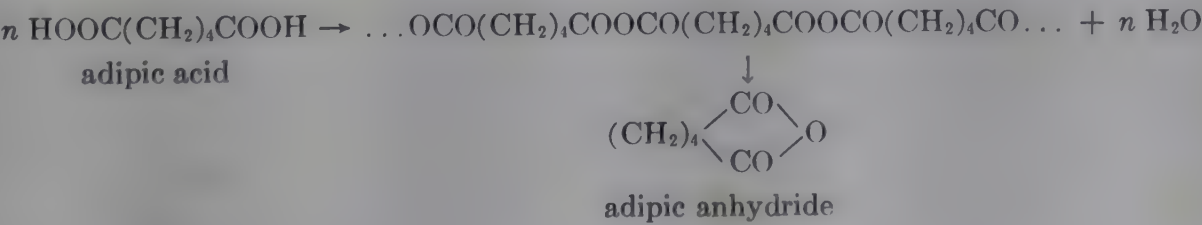
Under some conditions, carbon suboxide may also result.



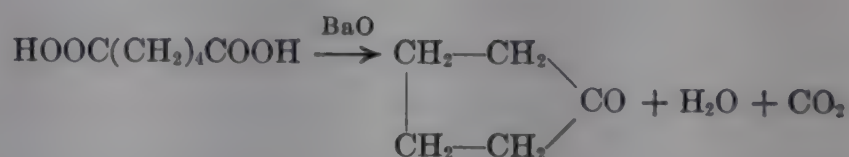
As the methylene chain increases, thermal decomposition increasingly induces ring formation. Thus succinic and glutaric acids, on heating or on removal of water by acetic anhydride or acetyl chloride, produce cyclic anhydrides.



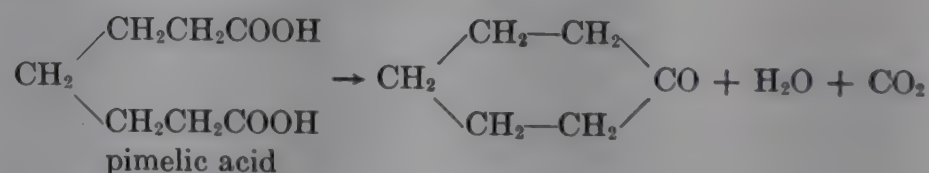
When adipic acid is heated, it gives a high-molecular-weight (polymeric) anhydride, but careful vacuum distillation of the polymer results in the unstable monomeric anhydride.



Cyclization together with decarboxylation is also possible. This occurs when adipic acid is heated in the presence of some metal oxides such as barium or thorium oxide as shown.

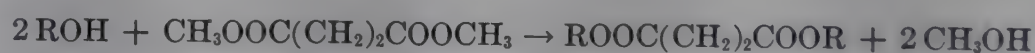


Pimelic acid is readily converted to cyclohexanone by this method, but this reaction is not used commercially since the ketone is obtained from phenol, or from cyclohexane, via cyclohexanol.

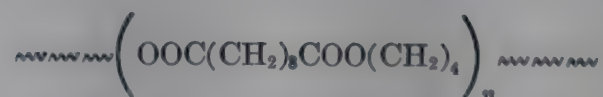


ESTERS, POLYESTERS, AND RESINS

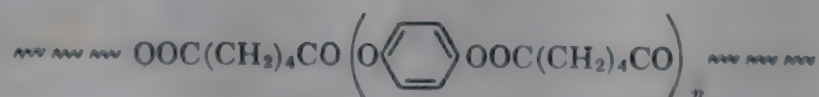
With Monofunctional Alcohols. This reaction is of extreme importance for the conversion of the dicarboxylic acids to the commercially important diesters. Esterification of the acids with alcohols in the presence of acid catalysts has led to a series of commercially important compounds. These materials are used as plasticizers, lubricants, and hydraulic fluids; oxidation under heavy load conditions is reduced by the use of thioethers and amines as antioxidants (8). Esters used in these applications include bis(3-methylbutyl) azelate, bis(2-ethylhexyl) adipate, and bis(2-ethylhexyl) sebacate (9). Esterification of the higher acids is normally accomplished by transesterification of the lowest alkyl (methyl, for example) diesters; this gives a smooth production of the higher-molecular-weight product.



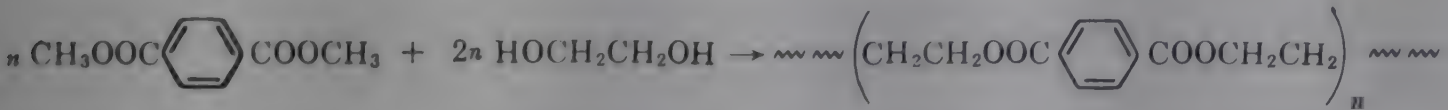
With Difunctional Alcohols. In the synthesis of polyesters, the carboxyl (or acid chloride) groups of the acid react with a difunctional alcohol (glycol). Catalysts are employed to increase the reaction rates (10); when aliphatic diols are reacted, acidic or basic catalysts prevent dehydration to an olefin. Several titanium salts are popular (11). The polyesters provide opportunities for obtaining widely varying properties in the final products by altering the nature of the reacting glycol and acid. When both are aliphatic, the products are solids which melt slightly above room temperature. Poly(tetramethylene sebacate) has a melt temperature of approximately 65°C (12).



With increasing aromaticity in the chain, the melting range of the polymer increases. Poly(1,4-phenylene adipate) prepared from hydroquinone and adipoyl chloride gives a product with a melt temperature of approximately 240°C (13).

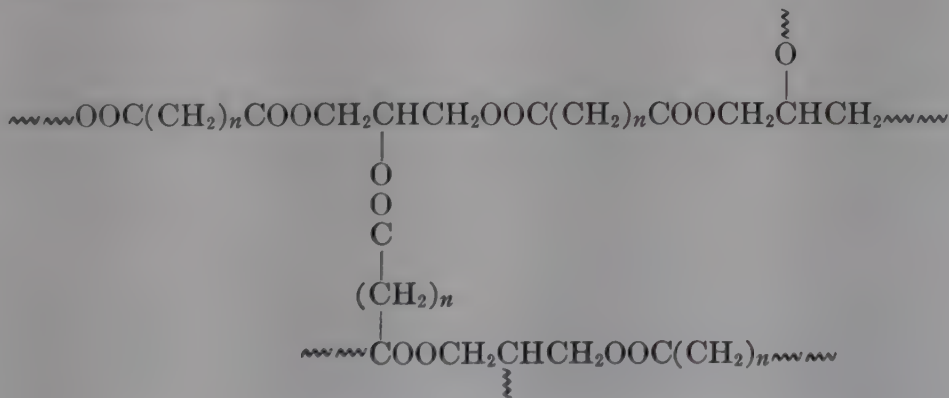


When bisphenol A (4,4'-isopropylidenediphenol, 2,2-bis(*p*-hydroxyphenyl)propane) or aromatic acids are used, the product is increasingly thermostable. For instance, poly(ethylene terephthalate) synthesized from ethylene glycol and dimethyl terephthalate has a polymer melt temperature of approximately 270°C (14).



The polyesters derived from aliphatic difunctional alcohols and aliphatic dicarboxylic acids are of relatively minor commercial importance despite the ability of several of these materials to form fibers and films; these materials lack the resilience of the tougher aromatic polyesters, which may even be synthesized in some cases by an anhydrous melt (rapid route) in contrast to the slower solvent reactions used for the aliphatic group.

With Trifunctional Alcohols. Thermosetting compounds are produced when a trifunctional alcohol such as glycerol reacts with a dicarboxylic acid, acid chloride, or ester. Prolonged heating of these materials gives an infusible resin which is insoluble in organic solvents owing to the large amount of crosslinking present. These alkyds (from the words alcohol and acid) are commercially important in that the degree of crosslinking may be controlled to a large extent before final molding and heat treatment to give a product with the desired degree of rigidity (or flexibility). Addition of other crosslinking agents to the polymer is not necessary as indicated by the following possible (idealized) network.



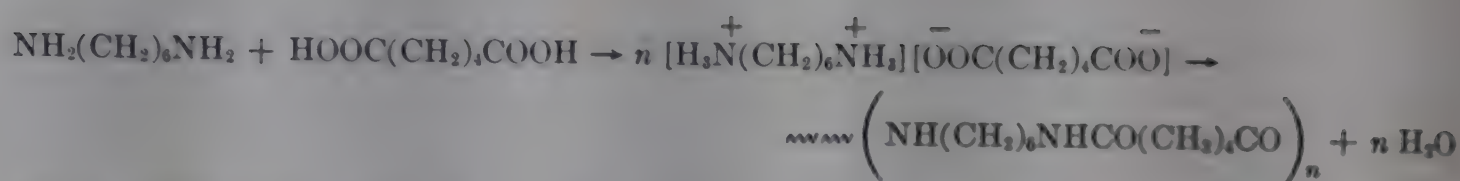
The various functional groups in the acid and the triol produce this three-dimensional system when reacted together in the correct stoichiometric proportions. Aliphatic acids employed include sebacic, adipic, and suberic.

POLYAMIDES

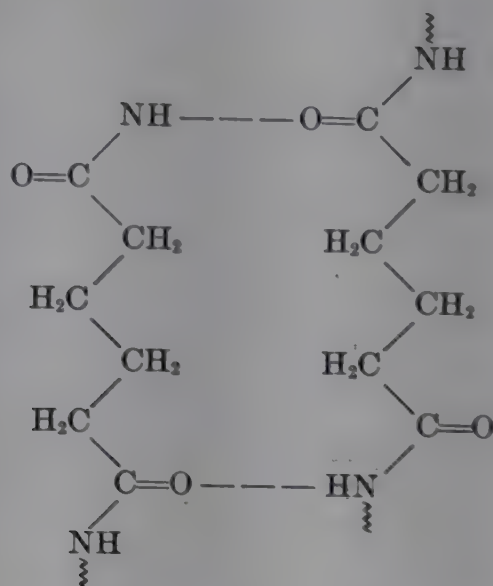
Aliphatic dicarboxylic acids and their derivatives (for example, acid chlorides) have proved to be extremely important in the condensation reaction with primary and secondary diamines to give a polyamide.



For industrial purposes, interest has centered on Du Pont's nylon-6,6 which is derived from adipic acid and hexamethylenediamine (15) and gives a material suitable for synthetic fibers, coatings, and elastomers.



Many possibilities exist for synthesizing polyamides from the several dicarboxylic acids and diamines available. Polyamides with varying numbers of methylene and other groups between the amide functionalities have been produced in limited quantities, but none has had the commercial impact of the first 6,6-nylon. The limited success of these efforts is due, in most part, to the unique structure of the 6,6-polyamide. Strong hydrogen bonding between chains and the distance between the functional groups is largely responsible.



Electron influence from the carbonyl of one chain is thought to extend to the amino group of another through the proton as shown. (See also Polyamides.)

Dicarboxylic Acid Production

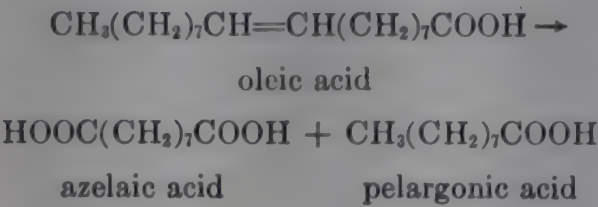
Commercial syntheses of the first five members of the series, oxalic to adipic, are mentioned under individual headings and are not considered here in detail. Generally, the acids are synthesized by controlled oxidation of available cyclic compounds, usually alcohols or ketones; this modern process has recently (1962) been extended to production of the twelve-carbon acid (16). Acids between C_7 and C_{12} were formerly obtained in quantity production by oxidation of linear precursors such as ricinoleic or capric acid. This method was expensive since mixtures of the acids were always produced which required extensive purification and separation.

Typical figures for the distribution products of dicarboxylic acids formed by the oxidation of monocarboxylic acids are shown in Table 4 (17). The nitric acid oxida-

Table 4. Nitric Acid Oxidation of Monocarboxylic Acids to Produce Dicarboxylic Acids

Acid oxidized	Acid product distribution, %						
	Succinic	Glutaric	Adipic	Pimelic	Suberic	Azelaic	Sebacic
enanthic, $\text{CH}_3(\text{CH}_2)_6\text{COOH}$	44	33	22	1			
caprylic, $\text{CH}_3(\text{CH}_2)_7\text{COOH}$	13	35	37	14	1		
pelargonic, $\text{CH}_3(\text{CH}_2)_8\text{COOH}$	15	22	32	22	6	3	
capric, $\text{CH}_3(\text{CH}_2)_9\text{COOH}$	13	14	19	24	17	11	2

tion of oleic acid, $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$, yields azelaic acid in relatively high yield, however. The oleic acid is attacked at the double bond to yield the azelaic acid. Azelaic acid can also be obtained by the ozone or chromic acid oxidation of oleic acid.



The raw materials (cyclic intermediates) that are used in the production of some dicarboxylic acids are given in Table 5.

Table 5. Cyclic Intermediates for Dicarboxylic Acid Production

Acid	Synthetic route	Number of carbon atoms	Raw material
glutaric	oxidation	5	cyclopentanol
adipic	oxidation	6	cyclopentanone
pimelic	oxidation	7	phenol
suberic	oxidation	8	cyclohexane
			cycloheptanone
			(suberone)
			cycloöctadiene
			(from butadiene
			or from cyclo-
			öctatetraene via
			acetylene)
dodecanedioic	ring oxidation	12	cyclododecatriene
			(from butadiene)

Acids with more than twelve carbon atoms have not been obtained from cyclic compounds. These tend either to be unstable or not available commercially. Many of the acids are synthesized from linear compounds containing a carbon skeleton similar to that required in the final product as shown in Table 6.

Table 6. Linear Intermediates for Dicarboxylic Acid Production

Acid	Synthetic route	Number of carbon atoms	Raw material
succinic	fermentation	4	ammonium tartrate ($\text{H}_4\text{NOOC}(\text{CH}_2\text{OH})_2\text{COONH}_4$)
pimelic	N_2O_4 oxidation	7	$\text{CH}_2(\text{CH}_2\text{CH}_2\text{CH}_2\text{OH})_2$ (18)
suberic	HNO_3 oxidation	8	castor oil (27)
azelaic	HNO_3 oxidation	9	castor oil (19)
sebacic	HNO_3 oxidation	10	castor oil (19)
isosebacic	catalytic sodium and butadiene	isomeric mixture of C_{10} acids	butadiene (20)
undecanedioic	oxidation	11	methyl oleate, 12-oxostearic acid (CdO catalyst) (21)

A recent trend in the chemical industry has been an increased interest in higher dibasic aliphatic acids to produce raw materials for polyamides, polyurethans, polyesters, and alkyds with a range of properties to supplant or supplement established materials. Esters of the higher acids have shown great promise in the field of heavy-duty lubricants, although there is a tendency toward the use of tribasic acid esters in this application. The prices of some of the more important acids over several years are shown in Table 7.

Table 7. Dicarboxylic Acid Prices (22)

Acid	Year	High, \$/lb	Low, \$/lb
adipic	1962	0.32	0.29
pimelic	1962	50 (approx) ^a	
suberic	1962	1.50 ^b	
azelaic	1962	0.37	0.36
	1961	0.40	0.36
	1960	0.40	0.40
sebacic	1962	0.655	0.655
	1961	0.67	0.65
	1960	0.655	0.655
	1959	0.655	0.655
dodecanedioic	1962	1.50 ^b	
tetradecanedioic	1962	high ^a	

^a Research chemical.

^b First year of quantity production; development use.

The above figures illustrate the availability and relative cost of the higher aliphatic dicarboxylic acids. Other dicarboxylic acids are not in quantity production but are available through normal consumer channels for investigational purposes. The C₈ and C₁₂ acids are offered in the hope that new nylons, plasticizers, and films will be developed which will provide stable outlets for these acids. Projections of future prices of these materials are always shown as tending toward the price of adipic acid, but these figures are dependent on high-volume, stable consumption.

Many of the dicarboxylic acids occur in plants and animals to a small extent, but in only a few cases has it proved economical to extract these on an industrial scale. Acids up to and including dodecanedioic have been detected in cow milk, buffalo fat, and hydrogenated fats. Salts of oxalic acid occur in plants and in human and animal urine. Malonic, succinic, glutaric, and adipic acids are found free in beets and various fruit juices. Higher dicarboxylic acids from suberic to docosanedioic, HOOC(CH₂)₂₀COOH, are obtained by oxidation of cork in which most of the acids occur as derivatives.

PIMELIC ACID

Pimelic acid (heptanedioic (IUPAC), 1,5-pentanedicarboxylic acid), HOOC-(CH₂)₅COOH, formula weight 160.17; water solubility 2.5 grams per 100 grams at 14°C; soluble in alcohol, ether; crystalline form monoclinic from water. The name pimelic is derived from the Greek word for fat, "pimele." The acid was first obtained by the oxidation of suberone (cycloheptanone), and is also produced by oxidizing capric acid, CH₃(CH₂)₈COOH, or oleic acid, CH₃(CH₂)₇CH=CH(CH₂)₇COOH (23). It may also be made from cyclohexanone by chlorination and conversion to the cyanide, followed by sodium hydroxide treatment; from salicylic acid by treatment with sodium in

amyl alcohol; from 1,1,5,5-pentanetetracarboxylic acid, $(\text{HOOC})_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{COOH})_2$, which on heating decarboxylates one carboxyl group from each end of the molecule to give pimelic acid. Nitric acid oxidation of animal fats also leads to pimelic acid, and this acid is found in trace amounts in the urine of herbivorous animals. Potential industrial syntheses of pimelic acid include the alkaline ring scission of potassium tetrahydrofurylpropionate to give the product in good yield (24).



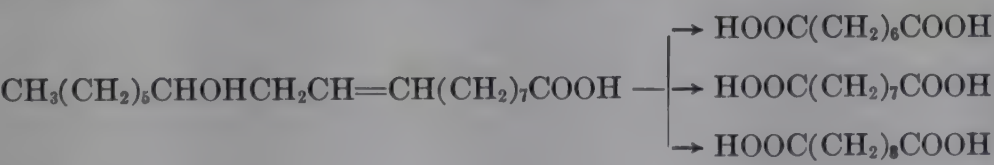
Alkaline scission of substituted cyclohexenes (25) and nitric acid oxidation of monocarboxylic aliphatic acids (see Table 4) are also potential sources.

Uses of Pimelic Acid and Its Derivatives. Pimelic acid has been incorporated into many polymeric systems of interest: with *cis*- and *trans*-1,4-cyclohexanediol and *o*-xylene- α,α' -diol it gives polyesters; other polyesters which could be used as plasticizers result from its interaction with hexanediol, 1,20-eicosanediol, and some polyglycols; with diepoxides it forms resins, and with *m*-xylene- α,α' -diamine or polymethylenediamines, polyamides are produced. Generally not much interest has been shown in the esters of this acid, but diallyl pimelate is used as a growth promoter for plants, and the dihydrazide of pimelic acid, $\text{H}_2\text{NHNOC}(\text{CH}_2)_5\text{CONHNH}_2$, shows bactericidal action against tubercle bacilli.

Several methyl-substituted pimelic acids are known but have not shown properties suited to industrial applications.

SUBERIC ACID

Suberic acid (octanedioic acid (IUPAC), 1,6-hexanedicarboxylic acid), $\text{HOOC}(\text{CH}_2)_6\text{COOH}$, formula weight 174.19; water solubility 0.16 gram per 100 grams at 20°C; soluble in alcohol; crystalline form long needles or irregular plates. The acid was first obtained by the oxidation of cork and derived its name from the Latin word “suber” for cork; it has also been recovered from plant stems, leaves, and wood by extraction with nitric acid (26). It is now obtained together with azelaic acid and sebacic acid by oxidizing ricinoleic acid from castor oil (glycerol ricinoleate). The



oxidizing agent for this reaction is nitric acid, and conditions favoring high yields of suberic acid are high temperature and relatively long oxidation period with dilute acid (27). The literature contains many claims for additives which will tend to increase the relative yield of the acids in this oxidation, but the acids normally require separation and purification by fractional distillation, in vacuo, of their methyl esters (28). Suberic acid has also been obtained from cyclooctene, C_8H_{14} , which is prepared by partial hydrogenation of cyclooctatetraene, C_8H_8 (produced by careful polymerization of acetylene) (29). Related to this process is the recent (1962) industrial production of suberic acid by oxidation of cyclooctadiene (obtained from butadiene). Another possible industrial-scale process for this acid is the conversion of 1,6-hexanediol with carbon monoxide under pressure to suberic acid in high yield (30). Suberic acid is present in the oxidation products from fish-liver oils and paraffins.

Uses of Suberic Acid and Its Derivatives. Suberic acid has been used in the manufacture of alkyd resins and polyamides. Condensation polymerization with diamines yields polyamides (31); the materials formed with hexamethylenediamine (nylon-6,8), or octamethylenediamine (nylon-8,8) have properties sufficiently different from those of the established polyamides (mainly nylon-6,6) to warrant large-scale production of suberic acid. Blends of these new polyamides may have greatly enhanced properties of elasticity, fiber-forming ability, and molecular flexibility compared with polyamides in use at present. Suberic acid also forms a polyamide with *m*-xylene- α,α' -diamine (32), and when the acid reacts with bicarbamic acid dihydrazide, a spinnable polymer results.

Esters of suberic acid are also commercially important. Diethyl and dibutyl suberate are used for plasticizers; the esters with aromatic alcohols are employed as lubricants in heavy-duty uses; suberic acid forms polyesters with polymethylene glycols; its dimethyl ester polymerizes with ethylene glycol to a material yielding fibers and elastic films; mixed polyesters with adipic acid, substituted and unsubstituted monocarboxylic acids, 1,4-butanediol, and suberic acid have rubberlike properties. When dimethyl suberate is mixed with vinylidene-vinyl chloride copolymers, nonblooming fibers result. Bis(2,3-epoxypropyl) suberate has been used as a stationary phase in gas chromatography.

AZELAIC ACID

Azelaic acid (nonanedioic acid (IUPAC), 1,7-heptanedicarboxylic acid), $\text{HOOC}-(\text{CH}_2)_7\text{COOH}$, formula weight 188.22; water solubility 0.2 gram per 100 grams at 15°C, 1.65 grams per 100 grams at 55°C; ether solubility 2.7 grams per 100 grams at 15°C; crystalline form leaflets or flattened needles; K (first) 2.88×10^{-5} at 25°C, K (second) 2.8×10^{-6} at 25°C. The name azelaic is derived from "azotic" (nitric) and elaidic (an acid stereoisomeric with oleic acid). It is found in many natural products which contain long-chain fatty acids and related compounds. These materials are converted by controlled atmospheric oxidation to mixed aliphatic dicarboxylic acids, often rich in azelaic acid. Octadecane, $\text{CH}_3(\text{CH}_2)_{16}\text{CH}_3$, paraffin oil, and paraffin wax all give azelaic acid on oxidation. Azelaic acid is obtained in yields of up to 35% from the crude ricinoleic acid obtained from saponification of commercial castor oil (19). The acid is dissolved in aqueous sodium hydroxide solution containing a 50% theoretical excess of alkali which is then treated with an aqueous (4 molar excess) potassium permanganate solution. This reaction is exothermic but is readily kept under control. The resulting potassium azelate solution is then acidified, filtered to remove manganese dioxide, concentrated, and finally the acid product is recovered. Potentially, a more efficient industrial synthesis of this acid may be the conversion of 1,7-heptanediol with carbon monoxide under heat and pressure to azelaic acid (yields for similar acids average about 80% by this process) (30). Other alternate methods for the preparation of this acid include nitric acid oxidation of ricinoleic acid (33–35), ozonization of oleic acid and decomposition of the ozonide (35), dichromate or sulfuric acid oxidation of dihydroxystearic acid (36).

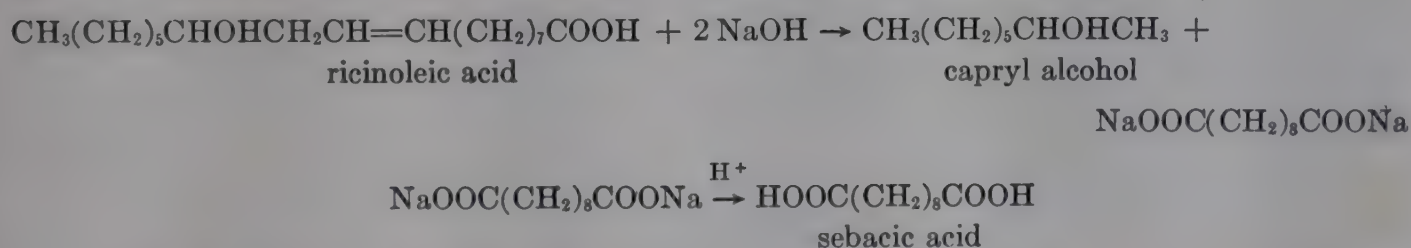
Uses of Azelaic Acid and Its Derivatives. The acid is used in hydraulic fluids and lubricants as a complex ester condensate with glycols and branched-chain alcohols. Aluminum salts of azelaic acid and stearic acid are used to thicken siloxane lubricating greases. Azelate esters mixed with diphenylsilanols are incorporated into high-performance lubricants. Bis(3,7-dimethyloctyl) azelate has been used as a

diffusion-pump oil. Bis(2-butoxyethyl) azelate is used to plasticize vinyl resins; similarly the bis(2-ethylbutyl) and bis(2-ethylhexyl) esters are used in lubricant blends (9) and as plasticizers in GR-S rubbers.

Azelaic acid derivatives are used widely in the plastics and synthetic fiber industries. With hexamethylenediamine the acid gives filaments when extruded into solutions of diisocyanates in silicone oils (37). In the presence of an acid catalyst (HCl), polymers of diethyl sebacate or diethyl azelate will undergo addition copolymerization with poly(methyl methacrylate). The dihydrazide of azelaic acid is used as a curing agent for epoxy resins.

SEBACIC ACID

Sebacic acid (decanedioic acid (IUPAC), 1,8-octanedicarboxylic acid), $\text{HOOC}(\text{CH}_2)_8\text{COOH}$, formula weight 202.24, forms colorless leaflets; water solubility 0.1 gram per 100 grams at 15°C; soluble in alcohol. This acid has been obtained by distillation of oleic acid, nitric acid oxidation of stearic acid, spermaceti, or ricinoleic acid, and by oxidizing many natural fats and oils (38). Commercially sebacic acid is manufactured by treating castor oil with caustic alkali at elevated temperatures. The caustic may be used in solid form, in aqueous solution, or suspended in a high-boiling organic liquid such as white mineral oil (39,40). With aqueous caustic, batch operations in an autoclave are often used in pressurized operations. In a related process, castor oil is slowly added to a caustic solution at 245°C in a kettle connected to a distilling column. The chief by-product, 2-octanol, passes off with some water vapor into a condensing system. The hydrogen gas evolved is vented and a separator returns the water to the reaction mixture, thereby maintaining a constant boiling point. After the run, the residue containing the alkali salt of sebacic acid is removed and dispersed in water. On acidification of the medium, sebacic acid is obtained as a fine white precipitate. Yields up to 40% of the castor oil input are obtained. Fatty acids of castor oil, mainly ricinoleic acid, give sebacic acid as shown:



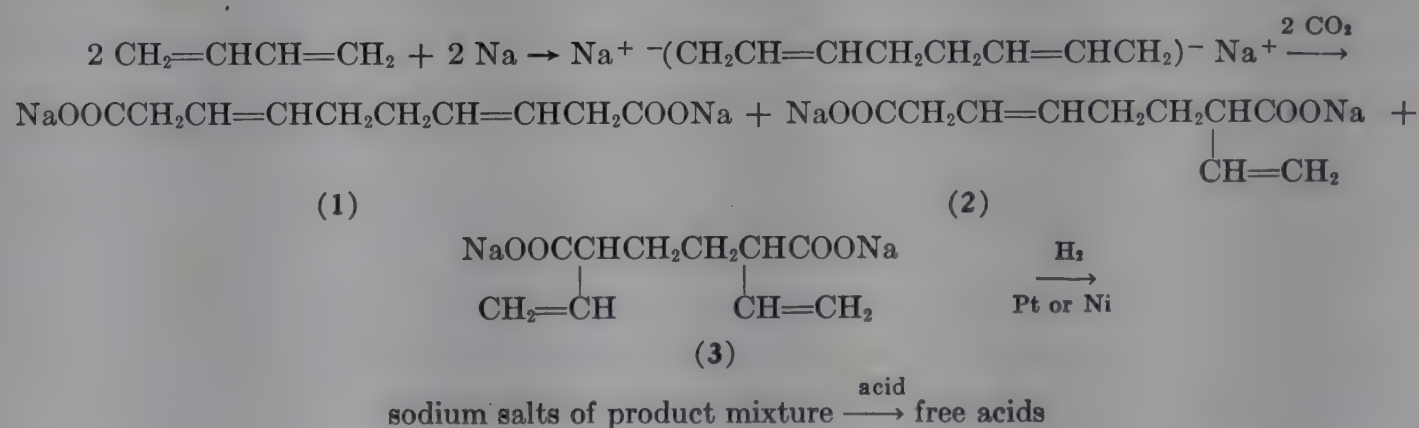
Uses of Sebacic Acid and Its Derivatives. Sebacic acid and related compounds are used in the plastics industry for plasticizers, alkyd resins, polyurethans, and urea resins, and in the field of synthetic lubricants for specialized applications (8,41,42). Bis(2-ethylhexyl or 2-ethylnonyl) sebacate diesters are used for aircraft lubricants, high-pressure applications, and as thinners for castor oil lubricants. For low-pressure applications, sebacate esters are mixed with metal soaps in many formulations. The esters are also stable plasticizers for poly(vinyl chloride) and other film-forming polymers, and their low toxicity makes them suitable for use in films for food-packaging applications. With polyglycols, sebacic acid forms polyesters such as polypropylene glycol sebacate, an extremely stable plasticizer which shows little tendency to migrate from the polymer in which it is incorporated. In alkyd resin applications, sebacic alkyds possess inherent flexibility characteristics which render them suitable for many applications that exclude more rigid alkyds—for example, textile coatings and paint

and lacquer systems. Sebacic acid also forms polyamide systems with ethanolamine or propanolamine and terephthalic acid.

ISOSEBACIC ACID

Isosebatic acid is the trade name given to a mixture of the following isomeric ten-carbon dibasic acids: sebacic acid, $\text{HOOC}(\text{CH}_2)_8\text{COOH}$; 2-ethylsuberic acid, $\text{HOOCCH}(\text{C}_2\text{H}_5)(\text{CH}_2)_5\text{COOH}$ (43); and 2,5-diethyladipic acid, $\text{HOOCCH}(\text{C}_2\text{H}_5)-\text{CH}_2\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{COOH}$ (44). This mixture is manufactured by U.S. Industrial Chemicals Company Division of National Distillers and Chemical Corporation (20). The product is a solid mixture of reasonably constant composition (not disclosed) in which 2-ethylsuberic acid predominates (45). Data on physical constants of mixtures should be approached with caution; data must always be determined for each batch before processing. Tentative specifications: C_{10} carboxylic acid content 98.5% minimum; volatile acids as acetic acid 300 ppm maximum; moisture 0.3% maximum; ash 0.05% maximum; iron 3 ppm maximum; iodine number 1.0 maximum; color APHA (20 grams in 100 ml methanol) 60 maximum; melting range 68–74°C; vapor pressure at 200°C, 2.9 mm Hg; at 250°C, 32.8 mm Hg; density at 80°C, 1.025 grams per ml; melt viscosity at 80°C, 78.5 cps; specific heat of vapor at 226°C, 0.34 cal per gram (estimated); heat of vaporization at 226°C, 107 cal per gram; specific heat of solid at 24°C, 0.33 cal per gram; heat of combustion 1296 kcal per mole; flash point (closed cup) 430°F; ionization constant at 25°C, $k_1 = 3.5 \times 10^{-5}$, $k_2 = 5.1 \times 10^{-6}$.

Manufacture and Uses. This material was initially produced on a commercial scale in 1957, based on a synthesis from a French patent (46) which employed metallic sodium and butadiene together with suitable catalysts. The first intermediate is disodioöctadiene, which then reacts with carbon dioxide to give sodium salts of the acid product, but these contain unsaturation centers, and the mixture must be reduced with hydrogen and a nickel or platinum catalyst before acidification to release the free acids:



A sodium dispersion, polycyclic hydrocarbon catalysts, and ethers in the reaction medium are all required for the process as described by the patent. The individual unsaturated acids are not separated on account of the large number of stereoisomers present: (1) has three cis-trans isomers; (2) has two cis-trans isomers, each of which is a racemic mixture; (3) has meso and racemic forms.

One promising application of this product is in the plasticizer field. Its esters with 2-ethylhexanol and with isoöctyl alcohol (see Alcohols, higher, synthetic), and its polyesters with poly(ethylene or propylene)glycols, give excellent plasticizers for vinyl and similar systems. Other applications are still being developed.

UNDECANEDIOIC ACID

Undecanedioic acid (IUPAC) (1,9-nonanedicarboxylic acid), $\text{HOOC}(\text{CH}_2)_9\text{COOH}$, formula weight 216.27, has not proved important in large-scale industrial practice, but some unusual applications have aroused interest. It is formed by auto-oxidation of methyl oleate or by catalytic oxidation of castor oil (47). A recent patent indicates undecanedioic acid can also be obtained by the action of sodium hydroxide and cadmium oxide on 12-hydroxyoctadecanoic acid (48). Undecanedioic acid (as well as other dicarboxylic acids having three to ten carbons) has shown complete suppression of ascites forms of lymphosarcoma in animals, and is under investigation for treatment of various cancers. Its esters with aromatic alcohols have potential in the plasticizer and lubricant fields.

6-Amino-2-octylundecanedioic acid, $\text{HOOCCH}(\text{C}_8\text{H}_{17})(\text{CH}_2)_3\text{CH}(\text{NH}_2)(\text{CH}_2)_4\text{COOH}$, has been used for polyester investigation work, and polyester amides have been prepared from the amino alcohol salts of this acid.

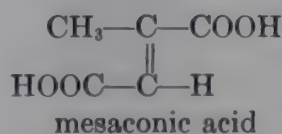
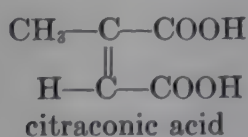
DODECANEDIOIC ACID

Dodecanedioic acid (IUPAC) (1,10-decanedicarboxylic acid), $\text{HOOC}(\text{CH}_2)_{10}\text{COOH}$, formula weight 230.3, was formerly obtained by oxidation of esters of fatty acids or by alkali fusion of hydrogenated castor oil. It has recently (1962) entered the early production stages on a commercial scale with the synthesis from butadiene via cyclododecatriene. It has been prepared by the peroxide treatment of cyclohexanone (49). Its dibutyl ester has been used as a plasticizer, and it may have many applications in the textile and leather field. As an intermediate, it may also have applications in the pharmaceutical, dyestuff, and insecticide fields.

OTHER DICARBOXYLIC ACIDS

Higher members of the series are known, but are only of chemical interest. Brassylic acid, $\text{HOOC}(\text{CH}_2)_{11}\text{COOH}$, mp 114°C , has been obtained by the oxidation of erucic acid, $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_{11}\text{COOH}$. Future large-scale production of the acids of this series in good individual yield would appear to depend on the emergence of syntheses suitable to volume production with low yields of side products, an increasingly difficult task with the longer chain acids. One such process may be the German route to aliphatic dicarboxylic acids from α,ω -diols reacted with carbon monoxide at high pressures and elevated temperatures (30).

Dicarboxylic acids with branched chains between the carboxyl groups are also known. (See Itaconic acid; Maleic acid, fumaric acid, and maleic anhydride.) Other dicarboxylic acids with branching and unsaturation are citraconic (methylmaleic) and mesaconic (methylfumaric) acids:



Itaconic, citraconic, and mesaconic acids are prepared from citric acid (qv) by distillation to the acid anhydrides; rapid distillation yields citraconic and itaconic anhydrides, and repeated distillation of the latter produces citraconic anhydride. Conversion to the acids is accomplished by heating with water or alkali.

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ACONITIC ACID, $\text{HOOCCH}_2\text{C}(\text{COOH})=\text{CHCOOH}$. See Citric acid.

ACRIDINE, $\text{C}_{13}\text{H}_9\text{N}$. See Heterocyclic compounds.

ACRIDINE DYES. See Dyes and dye intermediates.

ACROLEIN AND DERIVATIVES

Acrolein, $\text{CH}_2=\text{CHCHO}$, is the simplest member of the class of unsaturated aldehydes. α -Substituted acroleins, $\text{CR}_2=\text{CRCHO}$, are known where R represents alkyl or aryl groups. Acrolein and methacrolein (α -methylacrolein) are available on a large commercial scale. The extreme reactivity of acrolein is attributed to the conjugation of a carbonylic group with the vinyl group within its structure, and many of the advances in acrolein chemistry are a result of the methods used to control this extreme reactivity to give the desired products. Review articles and a book, respectively, have been published by Schulz and Wagner (1) by Ballard et al. (2), and by Smith (2a).

Acrolein is a clear, colorless, volatile liquid soluble in many organic liquids. At 20°C it is about 20%-by-weight soluble in water. Acrolein is a powerful lacrimator and a highly toxic chemical. Exposed to light and air, acrolein is rapidly polymerized. Commercial grades are stabilized by the addition of hydroquinone.

Some physical properties of acrolein and methacrolein are given in Table 1. Chemical reactions are shown below.

Table 1. Physical Properties of Acrolein and Methacrolein

Property	Acrolein	Methacrolein
molecular weight	56.06	70.09
specific gravity at $20/20^\circ\text{C}$	0.8427	0.8474
$\Delta \text{ sp gr}/\Delta \text{ temp}$	0.00116	0.00099
boiling point, $^\circ\text{C}$		
760 mm Hg	52.7	67.9
50 mm Hg	-9	3
10 mm Hg	-35	-25
vapor pressure at 20°C , mm Hg	215	119
freezing point, $^\circ\text{C}$	-87	-81
solubility at 20°C , % by wt		
in water	20.8	5.9
water in	6.8	1.7
refractive index, n_D^{20}	1.4013	1.4169

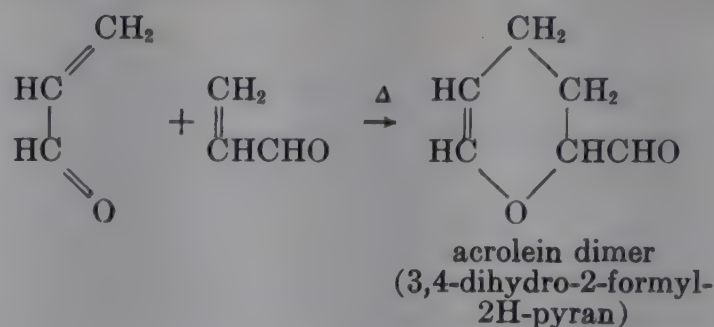
Reactions and Derivatives of Acrolein

Reactions Arising from the Conjugated Structure. Acting both as a diene and a dienophile, acrolein follows the Diels-Alder route in the formation of *acrolein dimer* (3). The physical properties of acrolein dimer, 3,4-dihydro-2-formyl-2H-pyran, are as follows: molecular weight, 112.12; sp gr at $20/20^\circ\text{C}$, 1.0776; bp at 10 mm Hg, 43°C ; vapor pressure at 20°C , 2.8 mm Hg; n_D^{20} , 1.4645; the compound sets to glass below -90°C .

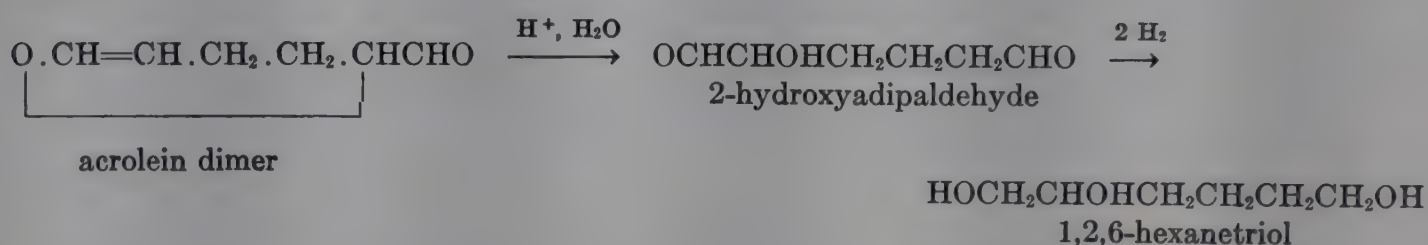
The dimerization rate is a function of temperature and dilution, and is not promoted by catalysts. The dimer is an extremely useful compound, but its formation during the course of other reactions could be detrimental. Fortunately, the dimeriza-

tion rate at room temperature is very slow and does not become important at temperatures less than 100°C.

Acrolein dimer provides a valuable starting point for the synthesis of chemicals useful in textile finishing, paper treating, and the manufacture of rubber chemicals, pharmaceuticals, plasticizers, and synthetic resins. Acrolein dimer is readily hydrated



at the carbon-carbon double bond and the starting material can be regenerated from the hydrate by distillation in the absence of acid catalysts. Hydrolysis of the dimer with ring rupture is swift and complete in the presence of an acid catalyst to give 2-hydroxyadipaldehyde (4). Hydrogenation of this dialdehyde leads to 1,2,6-hexanetriol.



2-Hydroxyadipaldehyde as a pure compound is a colorless liquid with a sharp odor. Because it rapidly polymerizes when highly concentrated to a white, water-insoluble material, it is supplied as a 25% aqueous solution which is stable, mild-odored, and relatively nonvolatile. Physical constants of the 25% aqueous solution are as follows: sp gr at 20/20°C, 1.066; vapor pressure at 20°C, 17 mm Hg; fp, -3.5°C; n_D^{20} , 1.3691; approximate pH, 3.0.

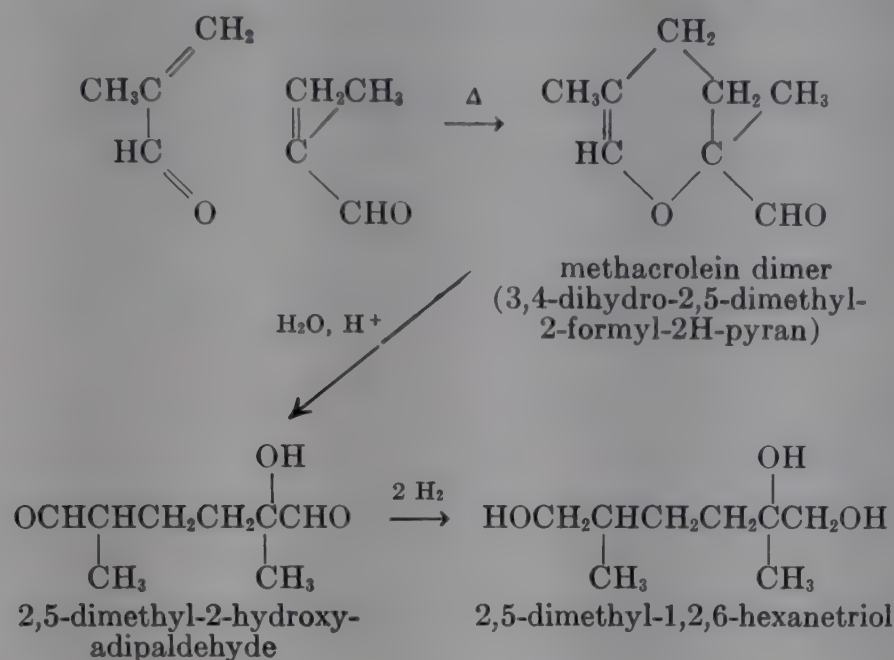
2-Hydroxyadipaldehyde reacts through crosslinking to insolubilize polyhydric materials, such as polyvinyl alcohols and polyvinyl acetal-type compounds, starch and cellulosic materials, and proteins, such as casein and animal glues. For example, with "Cellosize" hydroxyethyl cellulose, the use of proper reaction conditions permits the formation of films that are less soluble in hot and cold water than films formed with glyoxal. The films show only very slight color after curing for 2 min at 85°C. The reaction of 2-hydroxyadipaldehyde with proteins gives films similar in color and water resistance to those prepared with glyoxal.

1,2,6-Hexanetriol (see Alcohols, polyhydric) is a stable, colorless, high-boiling liquid useful as a softener and plasticizer for casein, zein, starch, dextrin, animal glue, cellophane, cork, and tobacco. As an intermediate it is of particular interest for the preparation of alkyd and polyester resins. Its simple esters have been suggested as special low-temperature lubricants.

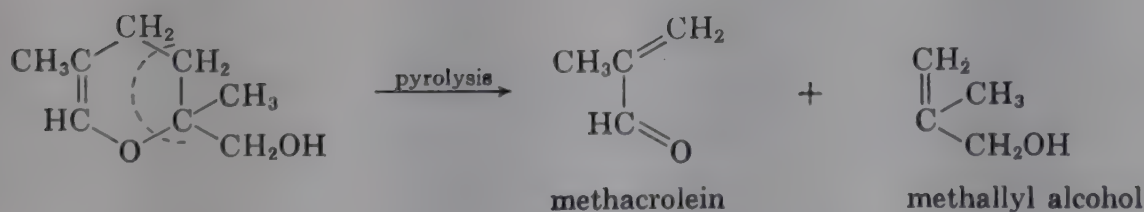
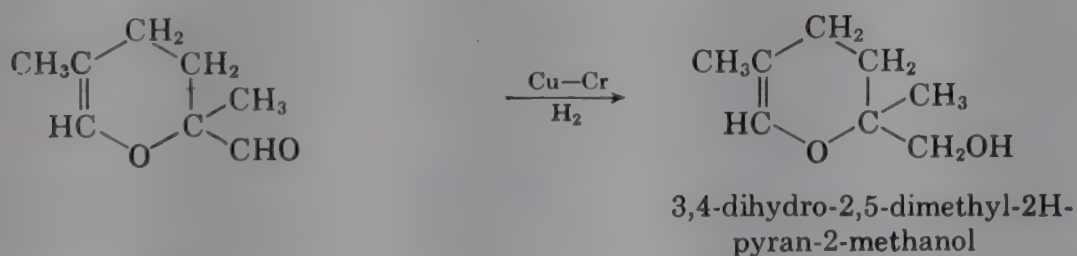
The reactions of methacrolein are analogous in many respects to those of acrolein but are modified somewhat by the presence of the methyl group in the alpha position. In the dimerization of methacrolein to form 3,4-dihydro-2,5-dimethyl-2-formyl-2H-pyran these principles apply (5). The dimerization rate of methacrolein is many times faster than that of acrolein. Likewise, in the reverse reaction, the pyrolysis of the

dimer to the monomer proceeds more readily in the case of methacrolein. The dimer of methacrolein is hydrolyzed somewhat less easily than acrolein dimer to give an analogous dialdehyde (6).

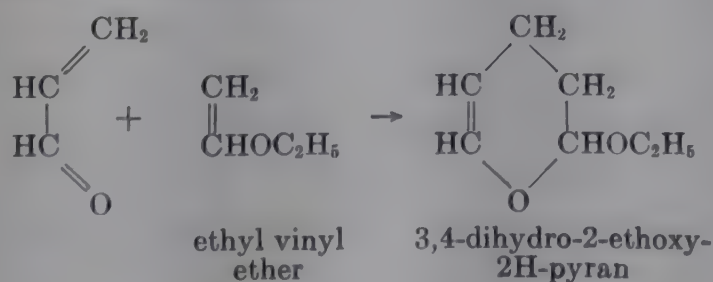
The hydrogenation of methacrolein dimer can be accomplished to give either one of two products. If a nickel catalyst is used, both the ring and the formyl group are hydrogenated to give 2,5-dimethyltetrahydropyran-2-methanol (7). If a copper-



chrome catalyst is used, the formyl group is hydrogenated but the unsaturation of the ring remains to produce 3,4-dihydro-2,5-dimethyl-2H-pyran-2-methanol (8). This product can be pyrolyzed to give methallyl alcohol and an equal molar quantity of methacrolein (9).

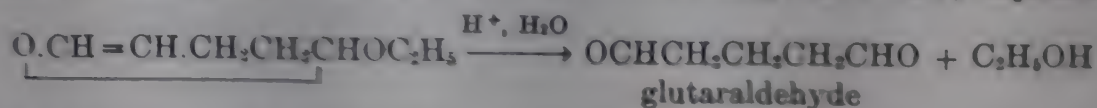


The Diels-Alder condensation of acrolein with alkyl vinyl ethers proceeds very swiftly (10). The competing dimerization of acrolein is not an important side reaction because of its relatively slow rate.



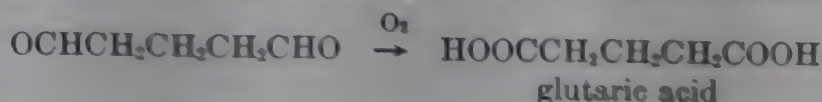
Physical constants of *3,4-dihydro-2-ethoxy-2H-pyran*: apparent sp gr at 20/20°C, 0.970; bp at 760 mm Hg, 142.9°C; vapor pressure at 20°C, 4.8 mm Hg; sets to glass below -100°C; 0.6% by weight soluble in water at 20°C; n_D^{20} , 1.4406.

Hydrolysis of *3,4-dihydro-2-ethoxy-2H-pyran* leads to *glutaraldehyde* (11) (see Glutaric acid). This product is available commercially as a 25% aqueous solution.

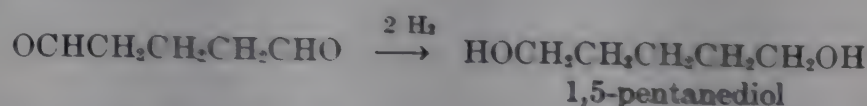


It is used as a crosslinking agent for proteins and polyhydroxy compounds, as a component of embalming fluids, and as a bactericide. Recent interest has been shown in glutaraldehyde as a leather tanning agent.

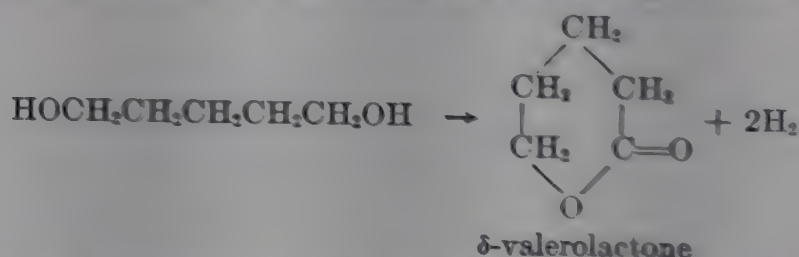
Oxidation of the dialdehyde produces *glutaric acid* (see Glutaric acid).



The reduction of glutaraldehyde is the source of *1,5-pentanediol* (pentamethylene glycol) (12) (see Glycols).

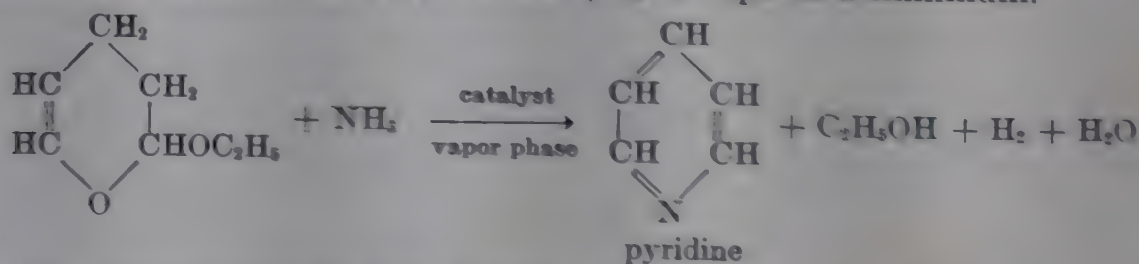


δ -Valerolactone is produced by the catalytic dehydrogenation of 1,5-pentanediol.

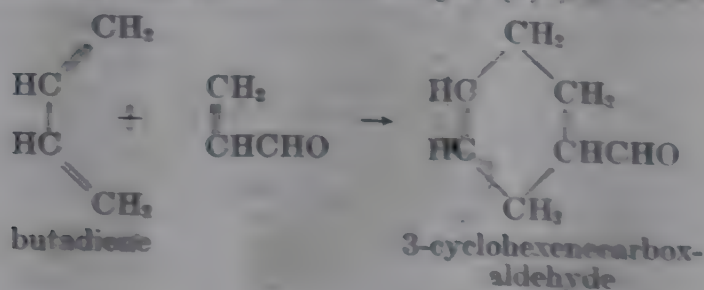


Physical constants: apparent sp gr at 20/20°C, 1.1102; bp at 50 mm Hg, 138°C; vapor pressure at 20°C, 0.05 mm Hg; fp, -10.4°C; n_D^{20} , 1.4571. The lactone is useful in the preparation of polyester resins.

The versatility of the acrolein-vinyl ether condensation product, *3,4-dihydro-2-ethoxy-2H-pyran*, is further illustrated by its conversion to *pyridine*; in this reaction, the formation of troublesome by-products (13) is kept to a minimum.

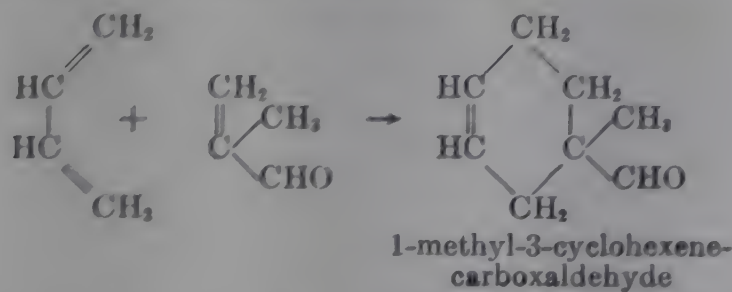


Further demonstration of the activity of acrolein as a conjugated molecule is its condensation in the Diels-Alder reaction, where it serves strictly as a dienophile (14). With butadiene it yields *3-cyclohexenecarboxaldehyde* (1,2,3,6-tetrahydrobenzaldehyde).

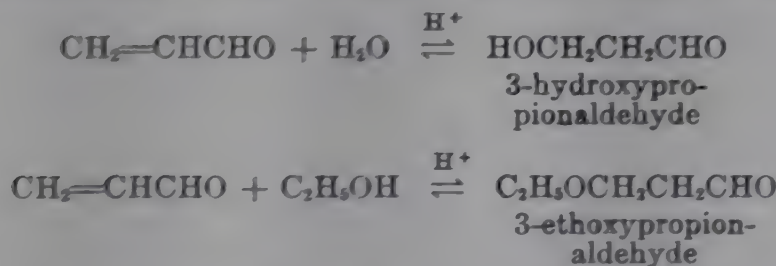


Physical constants: sp gr at 20/20°C, 0.9721; bp at 760 mm Hg, 164.2°C; vapor pressure at 20°C, 1.8 mm Hg; sets to glass below -100°C; 0.5% by weight soluble in water at 20°C; 1.0% by weight of water soluble in the aldehyde at 20°C; viscosity at 20°C, 1.8 cps; n_D^{20} , 1.4727. 3-Cyclohexenecarboxaldehyde, an unsaturated cyclic aldehyde, is an intermediate for the synthesis of pimelic acid (15).

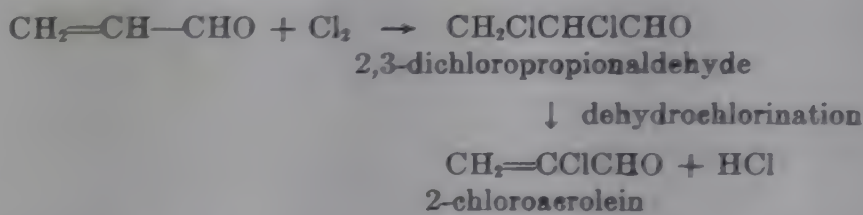
It is interesting that, in the condensation of methacrolein with butadiene, the extreme tendency of the substituted acrolein to dimerize is suppressed and good yields of the methacrolein-butadiene product are obtained.



Reactions Involving Addition to the Carbon-Carbon Double Bond. Some of the reactions of acrolein that depend upon the conjugated bifunctional character of the molecule have been discussed. The synthesis of many of the promising acrolein products, however, depends upon a precise control of reaction conditions to permit a reaction to proceed at one reactive site and not at the other. The addition to the carbon-carbon double bond is catalyzed both by acid and base. The additions of water (16) and alcohols (17) are examples. Such systems are in equilibrium, and special techniques are required to isolate the product in good yields because of the reversibility of the reactions. More complex reactions of acrolein with alcohols proceed under some conditions. These reactions will be found elsewhere in this article.



The addition of halogens to the carbon-carbon double bond is not complicated and proceeds readily. The addition of chlorine to form 2,3-dichloropropionaldehyde and the subsequent dehydrochlorination to give 2-chloroacrolein provides a synthesis of this extremely useful substituted acrolein (18).



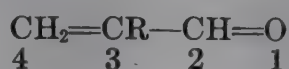
The chlorination of 2-chloroacrolein proceeds readily to form 2,2,3-trichloropropionaldehyde, $\text{CH}_2\text{ClCCl}_2\text{CHO}$ (19). Physical properties: apparent sp gr at 20/20°C, 1.489; bp at 760 mm Hg, 145°C; vapor pressure at 20°C, 5 mm Hg; sets to glass below -100°C; forms hydrate with water, containing 1 mole aldehyde and 1 mole water; n_D^{20} , 1.4798.

Table 2. Physical Properties of 2,3-Dichloropropionaldehyde and 2-Chloroacrolein

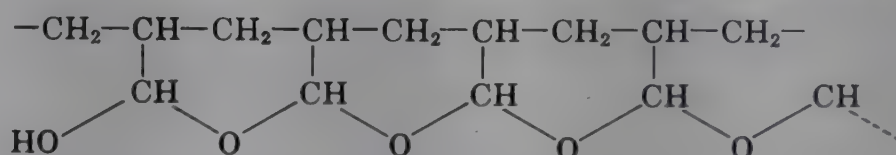
Property	2,3-Dichloro- propionaldehyde	2-Chloro- acrolein
molecular weight	127.01	90.48
specific gravity at 20/20°C	1.380	1.194
boiling point, °C		
20 mm Hg	55	
40 mm Hg		36
refractive index, n_D^{20}	1.4660	

Polymerization. In the absence of inhibitors acrolein polymerizes readily to an insoluble, highly crosslinked solid—referred to as *disacryl* in the early literature—which is of no use. Since 1957 much effort within the industry has been devoted to the problem of making commercially useful polymers of acrolein and methacrolein.

By modification of the reaction conditions and catalysts some variation in the type and properties of acrolein polymers may be obtained. Schulz and co-workers have published a series of articles dealing with such modifications and with some reactions of these polymers (20–26).



The unsaturated aldehydes can be numbered as shown, where R may equal either H for acrolein or CH₃ for methacrolein. Some experimenters have claimed that the polymerization proceeded via 3,4-addition, leaving pendent carbonyl groups on the polymer chain (27). Polymers of this type should be readily soluble in organic solvents. However, other researchers state that such polymerization occurs to only a minor extent; that a polymer chain forms, with the preliminary addition of a molecule of water; and that the structure therefore exists in the cyclic acetal form (28),



These workers state that any further reaction of the polymer proceeds through scission of the acetal linkage.

Homopolymerization of acrolein has been accomplished with many catalysts. Redox combinations, such as hydrogen peroxide/silver nitrate, potassium persulfate/sulfite and *tert*-butyl hydroperoxide/silver nitrate, have been used to produce polymer with some solubility in organic solvents (21). Other workers have used ultraviolet radiation (29), gamma rays (24), trialkyl phosphines (30), alkali and alkaline nitrates (37), organic peroxides (31), metal oxides (32), organic arsines (33), and piperidine (34) as catalysts for the polymerization. In most cases solutions of acrolein in organic solvents were employed. Emulsion polymerization, however, is said to give *polyacrolein* with superior qualities. The polymerization of a 50% emulsion of acrolein in water (prepared with the aid of emulsifying agents) gave a product with an average molecular weight greater than 50,000, which retained over 25 percent of the theoretical free carbonyl content (35).

Polyacrolein produced by any of the homopolymerization processes described thus far does not possess any outstanding properties. Different investigators have described the use of the material to form molded plaques and surface coatings. However, the

brittle nature of the polymer makes it unattractive for commercial applications. The polymer is soluble in aqueous solutions of sodium bisulfite or sulfur dioxide and the use of such solutions in the paper and textile industry has been proposed (26). Hydrogenation of an acrolein polymer gave a polyol with a hydroxyl equivalent weight of approximately 100 (33). Oxidation of an acrolein polymer with peracetic acid gave a polyacid (36). When polyacrolein was reacted with an aqueous solution of a strong base, a derivative of a poly(hydroxycarboxylic acid) was formed (37).

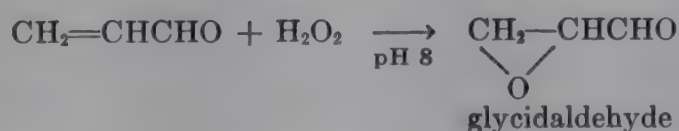
Copolymerization of acrolein with many other materials has been described. These include phenol (38), urea (39), sulfur (40), thiourea (39), acrylonitrile, acrylamide, methyl acrylate, vinyl acetate (23), styrene (41), 2-arylalkenes (42), allyl alcohol (43), maleic esters (44), and epoxides (45). Graft polymerization of acrolein onto previously formed polymers, such as polystyrene, poly(vinyl acetate), poly(vinyl chloride) and poly(vinyl alcohol), has also been accomplished (41).

Polymers of methacrolein have been made with properties which are far superior to those of polyacrolein. The desired 3,4-addition polymerization is promoted by conducting the reaction in the presence of finely divided silica in an aqueous mixture, using a redox catalyst system (46). The product is described as a colorless transparent plastic, which can be cast from solution into stiff films and sheets. It is soluble in dimethyl formamide. It is so heat-stable that it can be compression-molded at 250–305°C into clear films (52).

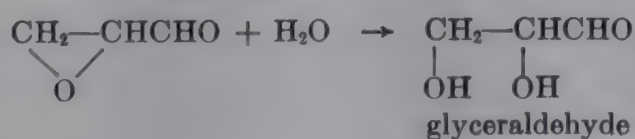
Methacrolein has also been copolymerized with many monomers. Copolymers of methacrolein with ethyl acrylate or butyl acetate are said to be substantially linear and to have properties which are somewhat superior to those of polymethacrolein (47). Methacrolein was copolymerized with styrene and the product was reacted with hydrogen cyanide to form polycyanohydrins (48). Similar copolymers were also hydrogenated to polyols (49). Compositions made by polymerizing methacrolein with butadiene can be vulcanized to form elastomers (50). Polymethacrolein or copolymers of methacrolein with olefinic compounds, when treated with aqueous sodium hydroxide, undergo an internal Cannizzaro reaction to give a product with alternating hydroxyl and sodium carboxylate groups (51). Products of this type have unusual surface-active effects and are proposed as emulsifying agents, detergents, and textile sizes.

In spite of the widespread efforts to make polymers of acrolein and methacrolein, no commercial products have yet been developed. It is possible that this situation will change and that polymers will provide an important outlet for the unsaturated aldehydes.

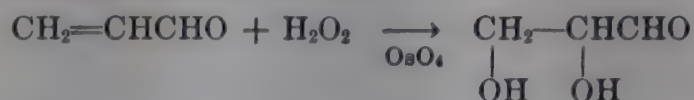
Reaction with Hydrogen Peroxide. If pH is controlled carefully during the reaction, acrolein can be converted to *glycidaldehyde* by the action of hydrogen peroxide (53),



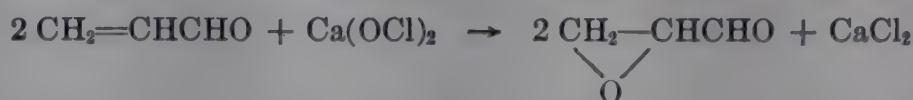
Excellent yields are obtained in this way and the reaction can be used as the first step in a synthesis of glycerol. The glycidaldehyde can be hydrolyzed, practically quantitatively, to *glyceraldehyde*, (54), and this compound can be hydrogenated to



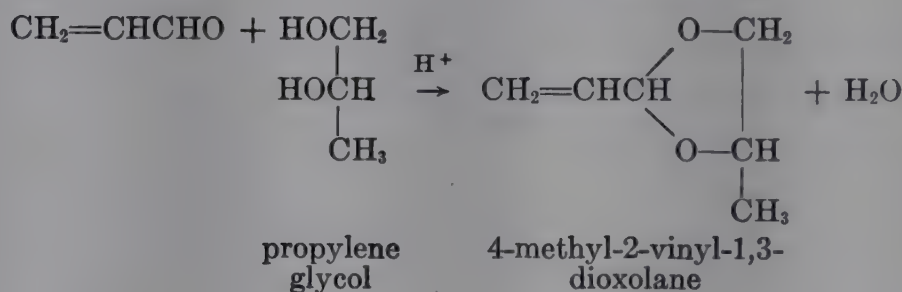
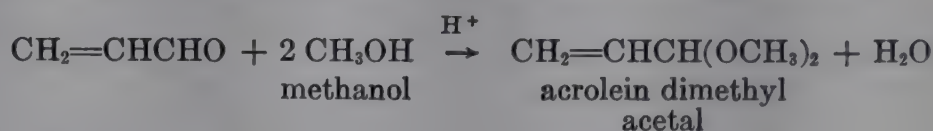
glycerol. If an osmium catalyst is used, acrolein can be hydroxylated directly to glyceraldehyde with hydrogen peroxide (55).



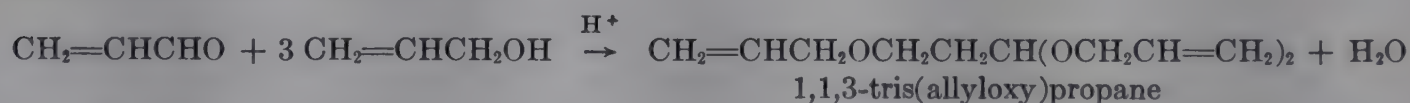
Reaction with Hypochlorites. Another route to glycidaldehyde is by the reaction of acrolein with metal hypochlorites. This reaction is carried out in aqueous solution and excellent yields are obtained if the pH is maintained in the proper range (56).



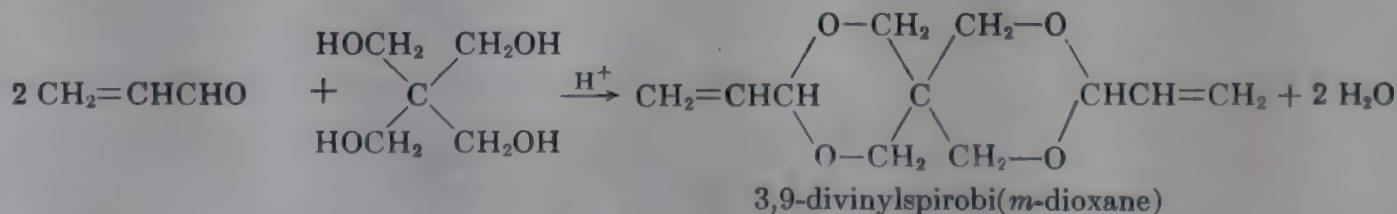
Reactions Involving the Carbonylic Group. The familiar aldehyde reactions proceed with rates accelerated by the conjugated structure. The *acetal-forming reactions* of acrolein are particularly interesting if it is desirable to preserve the vinyl unsaturation of the molecule. The acid catalyst required for the acetal reaction is also a catalyst for the addition to the carbon-carbon double bond. The reaction of the carbonylic group can be made to predominate (57) and, in the case of cyclic acetals, can be accomplished virtually to the exclusion of the competing reaction.



In certain cases the addition of alcohols to both sites is highly desirable and is readily accomplished. The addition of allyl alcohol thus gives a compound with several functional groups (58).



The ability of acrolein to form cyclic acetals while preserving the vinyl unsaturation is particularly important since it leads to a new class of thermosetting resins (1). The cyclic acetal resulting from the reaction of two moles of acrolein with pentaerythritol is known as *3,9-divinylspirobi(m-dioxane)* or *3,9-divinyl-2,4,8,10-tetraoxospiro(5.5)undecane*.

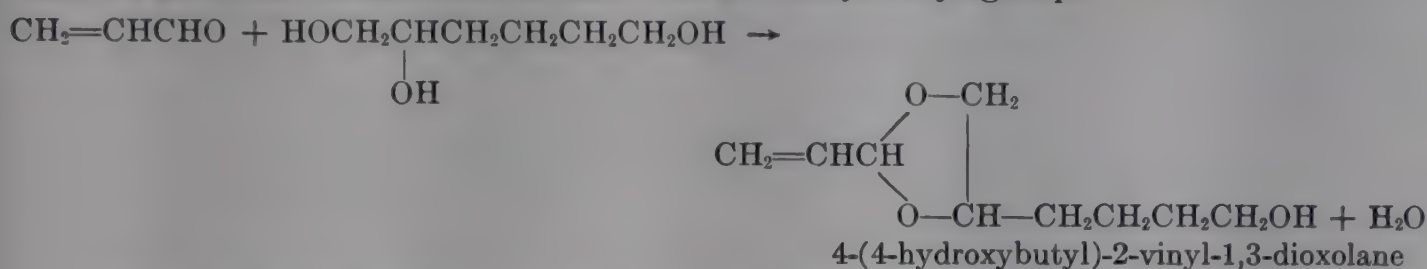


Physical constants: bp at 2 mm Hg, 120°C; mp, 43°C; density at 20°C, 1.251 g/ml; 1.4% by weight soluble in water at 20°C. The terminal vinyl groups of 3,9-divinylspirobi(m-dioxane) have a high order of reactivity with many active-hydrogen compounds. Of special interest is the affinity of these vinyl groups for alcohols.

In the simplest case, pentaerythritol can be reacted with the divinylspirobi(*m*-dioxane) to give a hard, tough, transparent resin.

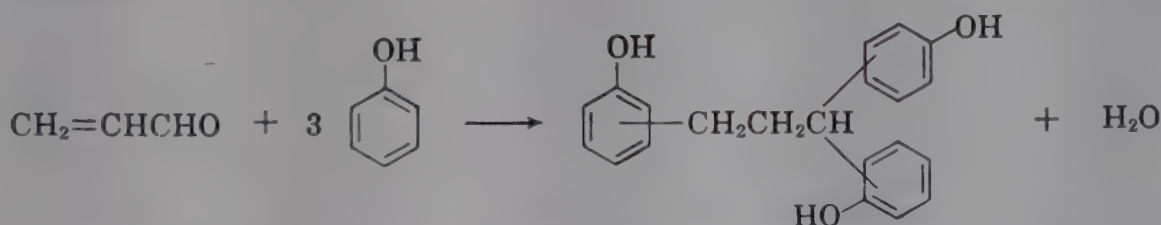
Comprehensive work dealing with the modification of resins of this type has appeared in the past few years (59). An important feature of this work was the discovery that phenols combine readily with the 3,9-divinyl-2,4,8,10-tetraoxospiro(5.5)-undecane to give polymers with excellent properties. It is believed that these compositions are formed by addition of the active hydrogens at the ortho and para positions of the phenol to the double bonds of the unsaturated acetal rather than by reaction of the hydroxyl group (60).

In a modification of this type of reaction, compositions are based on the acetal made from acrolein and hexanetriol. These compounds, which have recently been described, show great promise for use in metal coatings applications (61). The basic reaction gives an unsaturated acetal with a free hydroxyl group.



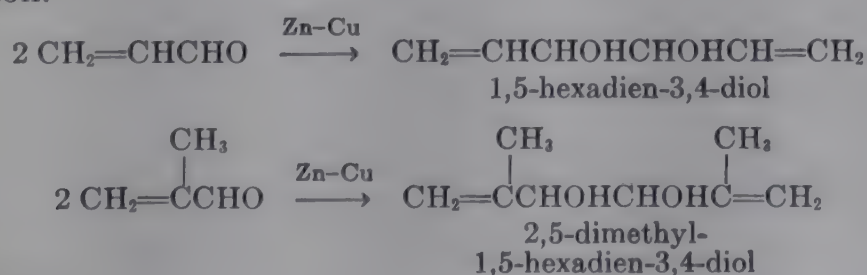
The acetal thus obtained is then reacted with dibasic acids and monomeric acids and the esters which are formed, mixed in the proper proportions, can be air-cured to give high-quality coatings.

An important reaction of acrolein which involves both the double bond and the carbonyl group is the reaction with phenol. With an excess of phenol, in the presence of an acid catalyst, 1,1,3-tris(hydroxyphenyl)propane is formed in high yield and efficiency (62).

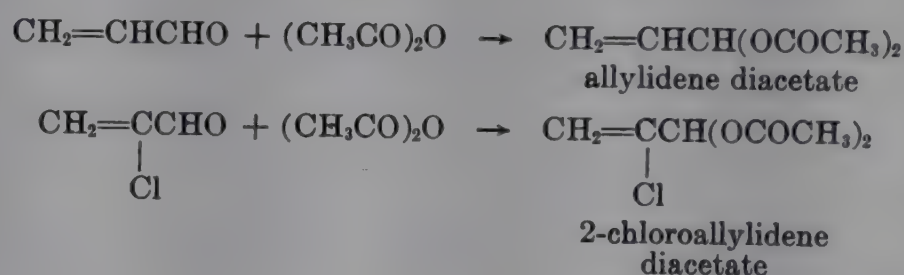


The product is a mixture of the possible isomers that can be formed by reaction of the phenol at the ortho and para positions. The tris(hydroxyphenyl)propane is used in producing special epoxy resins for very high temperature service and as a base for making polyethers for rigid polyurethane foams. This reaction with acrolein has also been extended to alkyl-substituted phenols (63). (See Alkylphenols.)

Through the influence of a zinc-copper couple, two moles of acrolein undergo a *bimolecular reduction* to give 1,5-hexadien-3,4-diol, which has an interesting combination of functional groups (64). The reaction is accomplished in an acid medium, and a stoichiometric amount of zinc is converted to a salt. Methacrolein undergoes an analogous reaction.

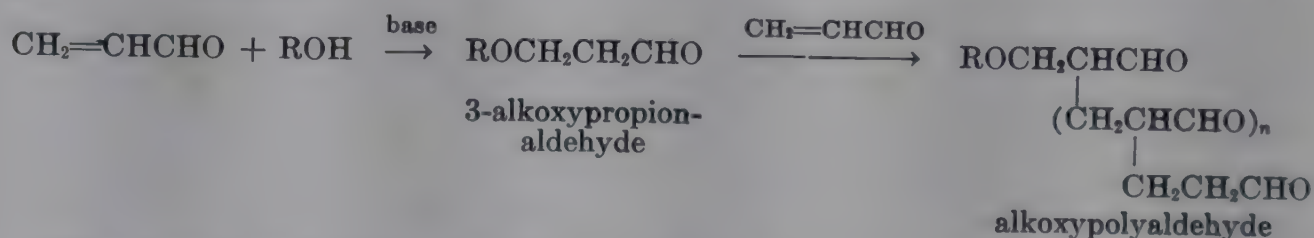


An important reaction of acrolein and 2-chloroacrolein is that with *acid anhydrides*. Acrolein and acetic anhydride under the influence of an acid catalyst give *allylidene diacetate* (65). The reaction of 2-chloroacrolein is analogous, giving *2-chloroallylidene diacetate*. Allylidene diacetate yields an interesting copolymer with vinyl chloride (66), but the copolymer of 2-chloroallylidene diacetate and vinyl chloride is of greater interest because of a more favorable polymerization rate. A large part of the vinyl chloride now used commercially is copolymerized with minor amounts of vinyl acetate to improve the behavior of the resin on the mill. The substitution of allylidene diacetate for the vinyl acetate markedly improves the service temperatures of the copolymers while still permitting the use of reasonable mill temperatures. Unfortunately, allylidene diacetate is the slower component in a vinyl chloride copolymerization and hence presents a problem in recovery of the excess monomer charged. 2-Chloroallylidene diacetate has all of the desirable characteristics of the unsubstituted compound as well as the important property of being the faster component in a vinyl chloride system.

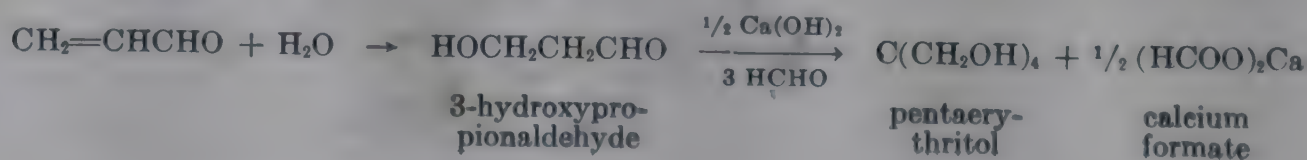


Physical constants of 2-chloroallylidene diacetate: apparent sp gr at 20/20°C, 1.2105; bp at 760 mm Hg, 212.1°C; vapor pressure at 20°C, 0.03 mm Hg; sets to glass below -60°C; 0.41% by weight soluble in water at 20°C; n_D^{20} , 1.4408.

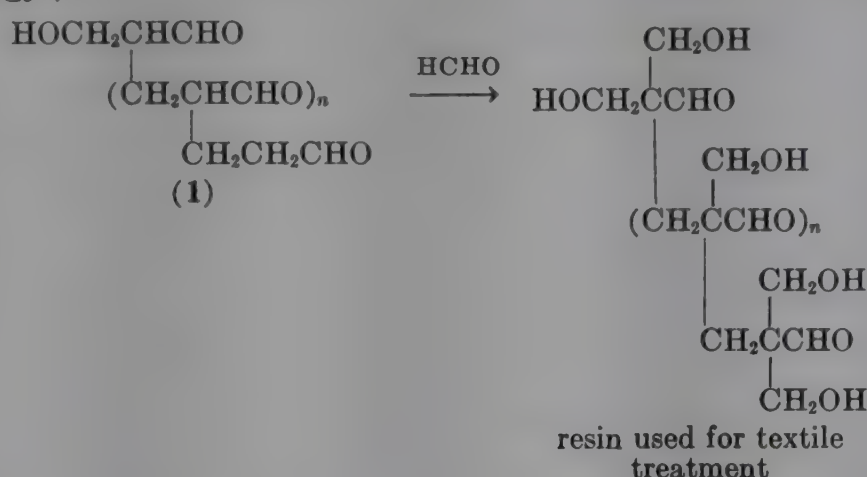
Base-Catalyzed Reactions. Most of the reactions previously discussed were acid-catalyzed in some form or another. The exception to this was the alternative use of a base in the addition of alcohols to the carbon-carbon double bond of acrolein. Such a reaction followed by a *Michael-type condensation* of additional acrolein leads to a useful variety of compounds. The Michael condensation proceeds quite readily without the use of alcohol, of course, but only resinous products have been obtained. By proper control of the condensation involving an alcohol, the desired number of units can be added to the carbon chain (67). In the case of methacrolein, the control of the Michael reaction is less critical and lower molecular weight products can be made to predominate (67a).



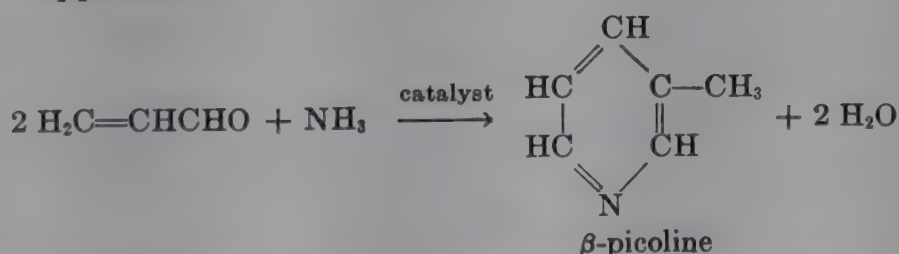
The reaction of acrolein with *formaldehyde* can be controlled to give *pentaerythritol* by using stoichiometric amounts of calcium hydroxide (68). The commercial synthesis of pentaerythritol by the use of acetaldehyde and formaldehyde is somewhat similar to this reaction. (See Alcohols, polyhydric.)



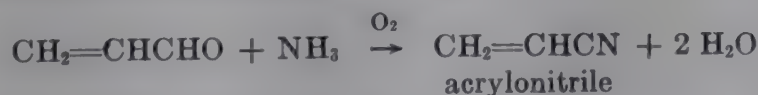
The pentaerythritol synthesis from acrolein is not competitive with the acetaldehyde-formaldehyde process but is a valuable aid in visualizing the sort of mechanism involved in the preparation of textile resins from acrolein and formaldehyde. The distinction here is the fact that catalytic and not stoichiometric amounts of base are employed. Thus, in the presence of catalytic amounts of base, the addition of methylol groups is accomplished while the original carbonylic groups of the acrolein are preserved. The polyfunctional character of the resin allows textile manufacturers to impart crease resistance, permanent shrinkage control, mildew resistance, and faster drying without the familiar drawback of chlorine retention in laundering (69). The formation of this resin is illustrated below. The first stage can be considered as a hydration of acrolein followed by a Michael condensation to give (1). The second stage shows the addition of methylol groups to complete the synthesis. (See also Textile technology.)



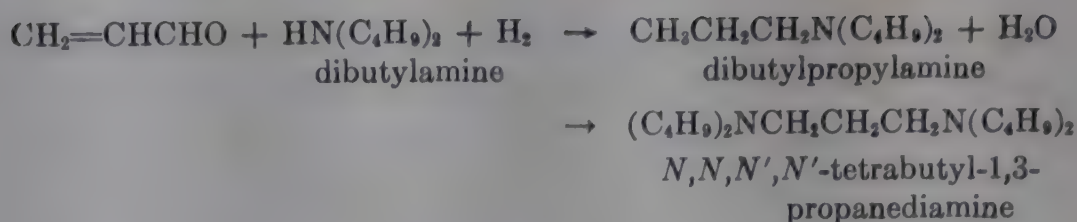
Reactions with Ammonia. The reaction of ammonia with acrolein in the liquid phase has given polymers which are of little interest (70). In the vapor phase, over a dehydration catalyst, acrolein reacts in a controlled fashion with ammonia to give good yields of β -picoline (2). This product could be an important source of nicotinic acid for dietary supplements.



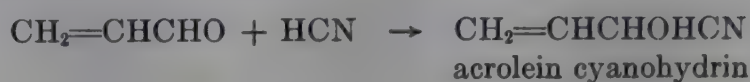
When the reaction is carried out over a molybdenum catalyst and in the presence of oxygen, ammonia reacts with acrolein to give acrylonitrile (71). This has been proposed as the basis for a commercial process.



Reductive Amination. In contrast to the liquid-phase reactions of acrolein and ammonia, the reductive treatment of acrolein with amines leads to useful products. It is significant that reactions with secondary amines are much more easily controlled than those with primary amines. Two types of products are obtained. In one case the amine adds only to the carbonyl. In the other case both reactive groups add the amine (72). The ratio of products can be controlled within limits by a proper choice of molar ratios.

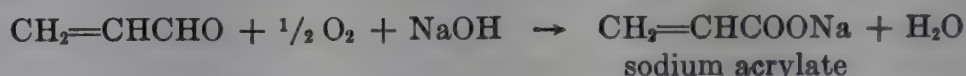


Reaction with Hydrogen Cyanide. The production of *acrolein cyanohydrin* requires a proper balance of reaction conditions since both hydrogen cyanide and the cyanohydrin require an acid stabilizer, whereas a basic catalyst is essential for the reaction. The sensitivity of acrolein to both acids and bases must also be considered in the determination of reaction conditions. The acrolein cyanohydrin is quite toxic and is a potent vesicant. While stabilized by the addition of an acid such as phosphoric, this acidity is likely to diminish to a hazardous level in extended storage through reaction with the cyanohydrin.

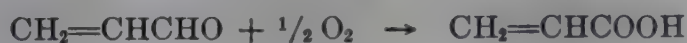


Physical constants of acrolein cyanohydrin: sp gr at 20/20°C, 1.0107; bp at 300 mm Hg, 165°C, at 50 mm Hg, 141°C; vapor pressure at 20°C, 0.03 mm Hg; sets to glass below -90°C; miscible with water; n_D^{20} , 1.4365.

Oxidation. Many attempts have been made to produce acrylic acid by the direct liquid-phase oxidation of acrolein. A practical process has never been developed because of the propensity of the compound to form peroxides which polymerize to worthless residues. As a way to avoid this, the so-called *Herstein process* was developed in which acrolein is oxidized with air in the presence of a silver oxide catalyst in a solution of sodium hydroxide (73). As the acrylic acid is formed, it is converted to the sodium salt. So far as is known this process has not been commercialized.



In 1959, 1960, and 1961, several processes were patented for the vapor phase oxidation of acrolein to acrylic acid (74). In all of these molybdenum catalysts are used and steam is employed as a diluent.



Manufacture

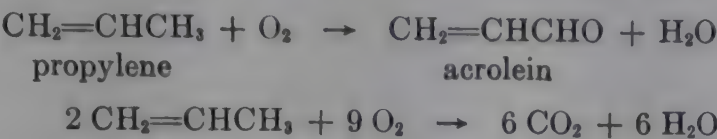
ACROLEIN

Acrolein can be manufactured on a commercial scale by the direct oxidation of propylene or by the cross-condensation of acetaldehyde with formaldehyde. Both processes are quite productive, and the choice of methods—based on comparative economics—might be governed by the ready access to raw materials.

Direct Oxidation of Propylene. A number of catalysts have been described for the oxidation of propylene to acrolein. These include cuprous oxide, mixed oxides of bismuth and molybdenum, mixed oxides of molybdenum and cobalt, oxides of antimony plus other metals, combinations including tungsten oxides, and a silver selenite composition promoted with cuprous oxide. Of this group supported cuprous oxide is believed to be the only catalyst used commercially.

A porous form of fused alumina is a suitable carrier for the cuprous oxide. The finished catalyst in the form of pellets or aggregate particles is placed within the tubu-

lar section of a vertically placed heat exchanger. Since the oxidation is exothermic, much of the heat is dissipated through the tube and is used to preheat the inlet gases. The principal reactions occurring within the converter can be represented as follows:



Other reactions occurring to a minor degree result in the formation of formaldehyde, acetaldehyde, propionaldehyde, and acetone. Since cuprous oxide rather than cupric oxide is the catalyst in this system, the partial pressure of the oxygen must be controlled relative to the propylene partial pressure to keep this catalyst essentially in the cuprous state. The desired reaction to give acrolein and water is favored over the chief competitive reactions when the propylene is present in excess of the oxygen.

A convenient means of supplying oxygen in concentrations less than that present in the atmosphere is to provide the unit with a recycle gas system. This practice returns part of the unreacted propylene to the catalyst zone in the course of the operation. Air from which the oxygen has been spent is mixed with fresh air and propylene to form the feed gas mixture. As an alternative, steam can be used to replace part of the recycled gas. The productivity of the system is a function of the relative concentrations of propylene and oxygen as well as of the mass velocity over the catalyst bed. The ability of the converter to dissipate the generated heat in the required reaction temperature range is a practical limitation on production rates. Operation of this system under moderate pressures to achieve the limiting mass velocities is an important factor in the design of the converter system. The reaction temperature varies with the activity of the catalyst but is usually in the range of 300–350°C.

The effluent gas from the converter passes through a cooler before being scrubbed with water. The scrubber system removes the acrolein along with the small amounts of propionaldehyde, acetone, acetaldehyde, and formaldehyde. The scrubber cycle gas containing nitrogen, propylene, carbon dioxide, and some oxygen is available to dilute the feed gases to the converter. To keep the inert gases at a suitable level, it is necessary to purge a portion of the scrubbed gases from the system. Since the purged gases contain propylene, it is advantageous to provide either a conventional propylene recovery system or a smaller catalytic single-pass system to convert much of the remaining propylene to acrolein under conditions more rigorous than those used in the larger converter. The acrolein, along with the by-product carbonylic compounds, is obtained as a dilute aqueous solution. The refining step is carried out by fractional distillation.

From a commercial standpoint the reaction conditions employed are likely to be dictated by productivity factors as well as a desire for maximum chemical efficiency. Under practical conditions, therefore, the efficiency of the oxidation can be expected to be somewhat below the 86% reported in the patent literature for rather special conditions (75).

A flow diagram of the propylene oxidation system appears in Figure 1. Propylene and air are fed into converter 1 along with recycled gases from the water scrubber 3. The converter effluent gases are cooled in 2 and scrubbed with water in 3. The acrolein and by-product carbonylic compounds are removed from the gas stream and pass into column 4. Here water and formaldehyde are removed from the base while acrolein with some acetaldehyde and minor amounts of propionaldehyde and acetone are

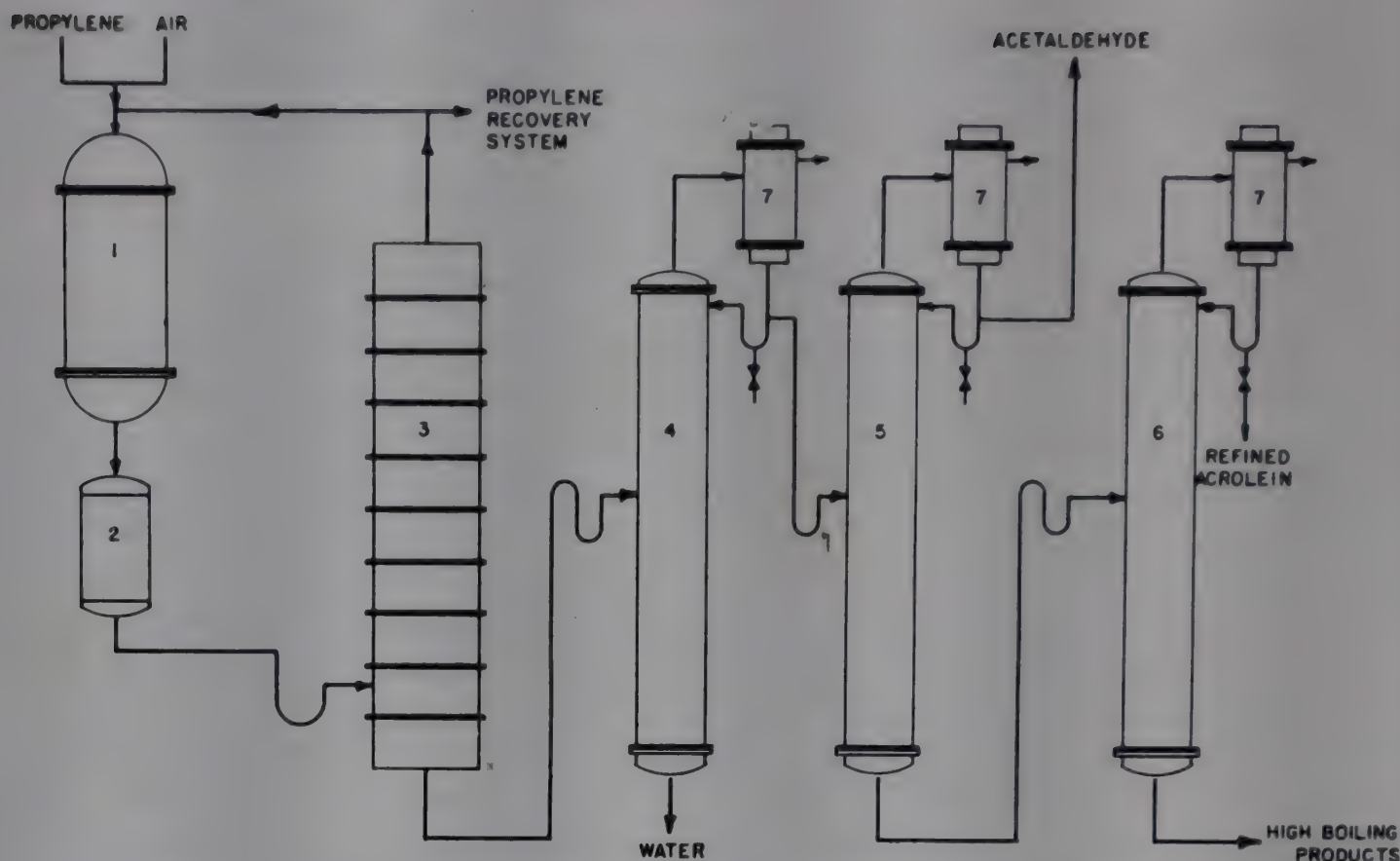
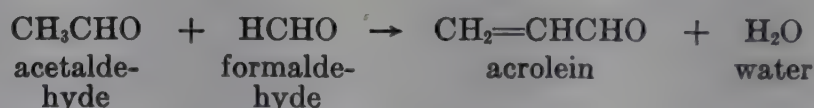


Fig. 1. Propylene oxidation system: 1, converter; 2, cooler; 3, scrubber; 4, 5, and 6, stills; 7, condensers.

removed as a distillate and pass to column 5. Here the acetaldehyde is removed as a forefraction. The acrolein with small amounts of propionaldehyde and acetone passes from the base of 5 into column 6. From the top of 6, refined acrolein is removed. Impurities are removed from the base.

Cross-Condensation of Acetaldehyde with Formaldehyde. This is a vapor phase reaction,



and can be accomplished by using the variety of catalysts generally associated with dehydration reactions. Lithium phosphate on activated alumina is a typical catalyst, as is sodium silicate on silica gel (76).

Acetaldehyde and formalin solution (aqueous 30% formaldehyde) are mixed in the proper proportions and fed to a vaporizer before entering the reaction zone. The catalyst in the form of pellets or sized particles is contained in a tubular converter for convenient transfer of heat. The reaction temperature is normally in the range of 300–350°C. The converter effluent is passed through a condenser before entering the refining system. Since the reaction is not favored by operation under pressure, converter inlet pressures of 10 to 25 psi, determined by the pressure drop throughout the system, are commonly used.

Of the two reactants, formaldehyde is the more difficult to recover as an unreacted component in the converter product stream. The mole ratio of the feed mixture is therefore adjusted to supply a slight excess of acetaldehyde to the catalyst zone. This reduces the unreacted formaldehyde to be recovered, but the excess acetaldehyde leads to increased amounts of by-product crotonaldehyde in the crude product.



Other identifiable by-products of the reaction are small amounts of methanol, propionaldehyde, and noncondensables consisting of carbon dioxide, carbon monoxide, and hydrogen. Tar formation, the chief factor in the efficiency loss, is responsible for a loss of catalyst activity. The gradual decline in catalyst activity usually makes reactivation economical after about 150–200 hr. Treatment of the fouled catalyst with air and steam at 400°C is particularly effective in removing the carbon deposition. While the conversion declines gradually during the course of the reaction cycle, average efficiencies of about 75–80%, based either upon the formaldehyde or the acetaldehyde, are observed. The single-pass yields based on formaldehyde are 20–50%.

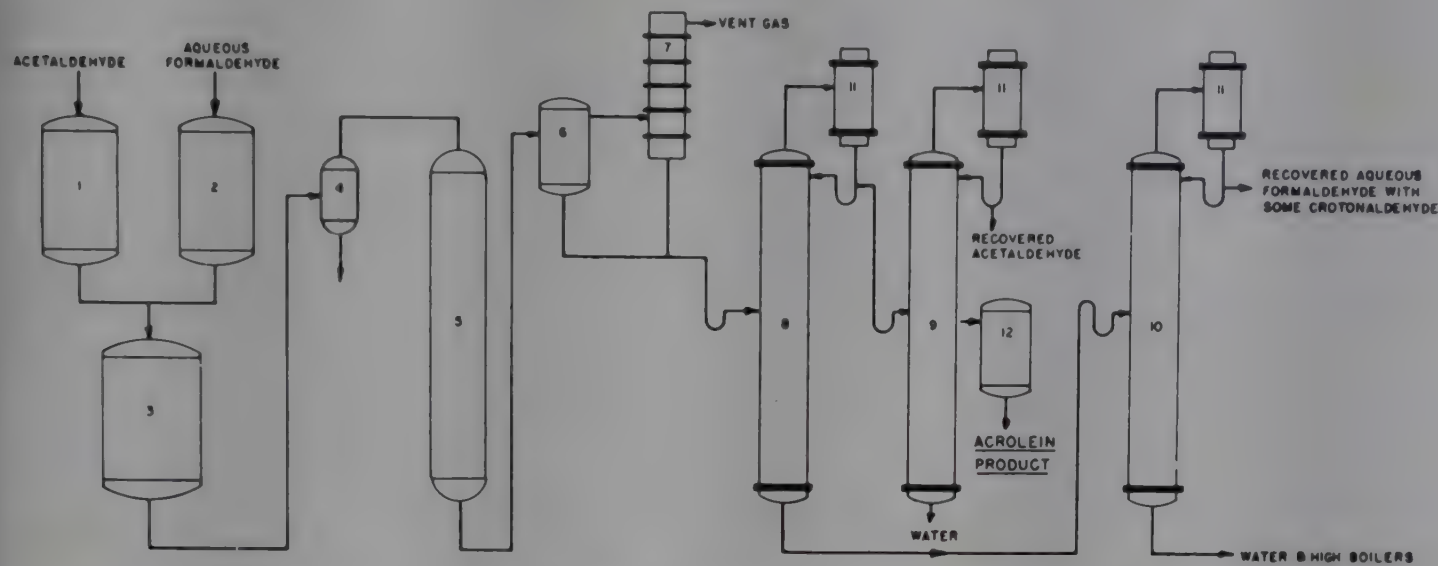


Fig. 2. Cross-condensation process: 1 and 2, storage tanks; 3, feed tank; 4, vaporizer; 5, converter; 6, cooler; 7, scrubber; 8, 9, and 10, stills; 11, condensers; 12, cooler.

A flow diagram of the cross-condensation process appears in Figure 2. Acetaldehyde and aqueous formaldehyde are fed from 1 and 2 to prepare a proper feed mixture in 3. The feed solution is vaporized in 4 and passed over the catalyst in converter 5. Condensables are removed in cooler 6. The noncondensables pass into water scrubber 7 and are discarded. The scrubber water from 7 is combined with the condensate from 6 and fed into column 8 at atmospheric pressure. From the top of 8 is removed a mixture of acetaldehyde, acrolein, and water. This is passed into the side of column 9 where acetaldehyde is removed overhead at atmospheric pressure. Refined acrolein is removed from the side of 9 below the feed point. From the base of column 8 are removed formaldehyde, crotonaldehyde, water, and high-boiling materials. These are passed into a pressure column 10 to recover aqueous formaldehyde overhead as a distillate along with some crotonaldehyde. This is recycled to the converter feed tank. From the base of 10 are removed water and residues.

Production and Price. Acrolein was manufactured by the cross-condensation process on a small commercial scale in Germany during World War II. Some time later it was offered by the Shell Chemical Corporation and Union Carbide Chemicals Company, a division of Union Carbide Corporation, in limited quantities as an experimental compound. Large-scale commercial facilities were first operated by Union Carbide Chemicals in 1952 and their scale of operation has expanded greatly since that

time. A large-volume plant was installed in 1959 by Shell Chemical Corporation to provide starting material for a new glycerol process.

On May 1, 1961 the selling price for acrolein in tank car lots was 31¢/lb. There is considerable evidence that the price will be lower in the near future.

Physiological Properties. Acrolein is a highly toxic chemical and is poisonous by ingestion, inhalation, and absorption through the skin. The LD_{50} for rats as a single oral dose is in the order of 0.05 g/kg. Acrolein is quite irritating to the eyes, respiratory tract, and lungs and should be handled in a closed reaction system or under conditions that provide ample ventilation. Exposure to 1 ppm in air causes detectable eye and nose irritation in 2–3 min. The maximum allowable concentration for an 8-hr exposure has been estimated at 0.5 ppm. For comparison similar values have been set for chlorine and carbon disulfide at 1 ppm and 20 ppm, respectively. The irritating effect of acrolein at very low concentrations usually gives adequate warning before exposure to toxic quantities can occur.

Handling and Storage. To retard the polymerization of acrolein, 0.1–0.25% of hydroquinone is added as an inhibitor. Shipments are made in tank cars and drums from which oxygen has been excluded. Acrolein thus prepared and stored under average conditions polymerizes to the extent of less than 1% per month. Acrolein from which the stabilizer has been removed polymerizes exothermically to give an insoluble, crosslinked resin. Methods of handling should take into account not only the toxic nature of acrolein, but must include such precautions as are usually accorded a flammable organic chemical. In addition, care must be exercised to preclude the possibility of contaminating the acrolein in storage. Basic materials may initiate polymerizations that may be hazardous. Strong acids may also catalyze polymerizations of a rapid nature. Iron or steel are satisfactory materials of construction for handling inhibited acrolein. Copper metal or its alloys in distillation systems is recommended because of the additional inhibiting effect conferred by this material.

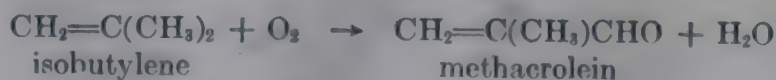
Analyses and Specifications. Commercial-grade acrolein has a minimum purity of 92% and contains 0.1–0.25% hydroquinone inhibitor. The chief impurity is water, which should be 4.0% or less. Saturated carbonyls, chiefly acetaldehyde and propionaldehyde, make up most of the remainder. Hydroquinone is determined by a colorimetric procedure involving its reaction with pyrrole in the presence of an oxidizing agent.

The total of acrolein and saturated carbonyls (the latter calculated as acetaldehyde) is determined by the hydroxylamine hydrochloride method of analysis. Acrolein is determined independently as an unsaturated compound by use of the bromine-bromide reagent. The carbonylic impurities expressed as percent acetaldehyde are obtained by difference. Water in commercial-grade acrolein is determined through the use of the Karl Fischer reagent.

METHACROLEIN

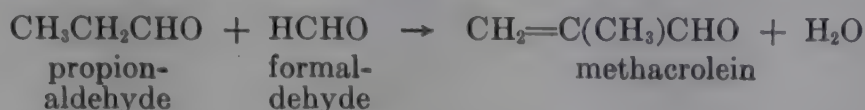
Methacrolein can be prepared commercially by the direct oxidation of isobutylene or by the cross-condensation of propionaldehyde and formaldehyde. The processes employed are completely analogous to those outlined for the manufacture of acrolein.

The oxidation processes in which the cuprous oxide catalyst previously described is used can be represented as follows:



In general the catalytic reaction of isobutylene with oxygen can be accomplished at a somewhat lower temperature than the analogous reaction of propylene. Perhaps as a result of this fact the overall efficiency of methacrolein production is measurably higher than that of acrolein.

The reaction of propionaldehyde with formaldehyde in the vapor phase cross-condensation process can be used to prepare methacrolein. The method employed can be quite similar to that described for the preparation of acrolein.



This process is quite productive and can be operated with an efficiency similar to that observed in the reaction of acetaldehyde and formaldehyde.

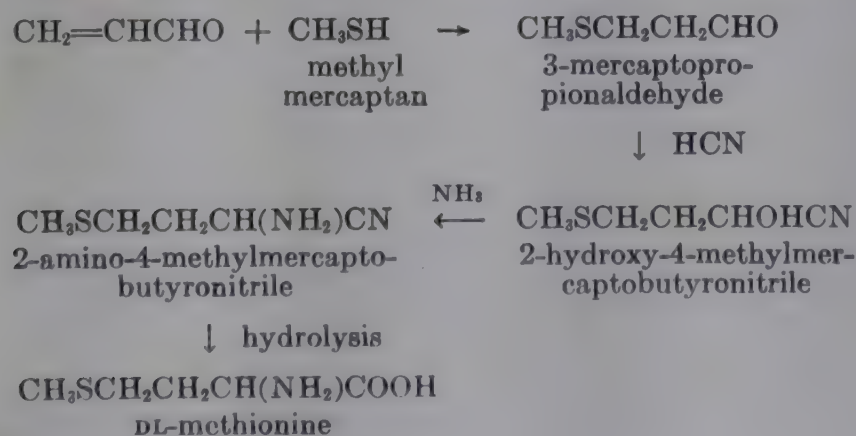
Methacrolein was introduced on a limited commercial scale at about the same time as acrolein. Both the Shell Chemical Corporation and the Union Carbide Chemicals Company have long listed methacrolein among their experimental chemicals. Large-scale commercial lots have been available from the latter source since 1952. The Union Carbide Chemicals Company on July 1, 1961, priced methacrolein at \$1.00/lb for less than carload lots of drums, fob Institute, W.Va. As the use of methacrolein develops, it can be expected that prices of large shipments will be substantially reduced.

Physiological Properties. Methacrolein, although quite toxic, is somewhat less so than acrolein. Since its vapor pressure is somewhat lower than that of acrolein, its effect as a lacrimator is not quite as powerful. The precautions recommended for the safe handling of acrolein may well be applied to the use of methacrolein.

Uses

Relatively large quantities of acrolein are consumed in the manufacture of several of the derivatives described in the preceding sections. These include 1,2,6-hexanetriol, hydroxyadipaldehyde, and glutaraldehyde. At the present time (1962) the quantity converted to glycerol via glycidaldehyde is not known.

One of the largest single uses for acrolein in 1962 is in the production of methionine (see Amino acids) by a process similar to the one outlined below (77). This synthetic amino acid, which now sells at about \$1.43/lb, is added to certain chicken feeds at the rate of a pound (or less) per ton. The use of methionine for this purpose results in improved feeding efficiency and accelerated chick growth. Methionine is also used to fortify commercial dog food. Investigations have been under way for several years to determine the economics of supplementing swine and ruminant feeds with



methionine. The indications are that the use of methionine in commercial feed formulations will continue to grow at a rapid pace. Fortunately, the racemic (DL) methionine is as effective as the naturally occurring L-isomer for the maintenance of a positive nitrogen balance and of proper growth in man and animals. There is increasing evidence that many familiar foods for human and animal consumption are so limited in their methionine content that fortification might be considered.

Other uses for acrolein that occupy a significant portion of the annual production center about its several resin applications. Various promising applications for methacrolein in polymers are also being developed.

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 Union Carbide Chemicals Company

ACRYLAMIDE

Acrylamide, $\text{CH}_2=\text{CHCONH}_2$, formula weight 71.08, is a white, crystalline solid which is assuming increasing industrial importance as a chemical intermediate and as a monomer. Acrylamide is highly water-soluble and tends to impart this same property to polymers and copolymers. Polyacrylamide is especially useful as a flocculant for fine solids suspended in water, as a thickening agent, and as a pigment retention aid in papermaking. Copolymers of acrylamide are being used in chemical grouts, in surface coatings, and in additives to increase the dry strength of paper. (See also Acrylic acid and derivatives.)

Properties

Physical Constants (1,2)

melting point.....	$84.5 \pm 0.3^\circ\text{C}$
vapor pressure.....	0.007 mm at 25°C 0.033 mm at 40°C 0.07 mm at 50°C
boiling point.....	87°C at 2 mm 103°C at 5 mm 125°C at 25 mm
heat of polymerization.....	19.8 kcal/mole
density.....	1.122 g/ml at 30°C
crystal system.....	monoclinic or triclinic
crystal habit.....	thin tabular to lamellar
refractive indexes	
n_x	1.460 (calcd)
n_y	1.550 ± 0.003
n_z	1.581 ± 0.003
optic axial angles.....	2E 98° , 2V 58°
optic sign.....	(—)

Solubilities (2) in g/100 ml solvent at 30°C

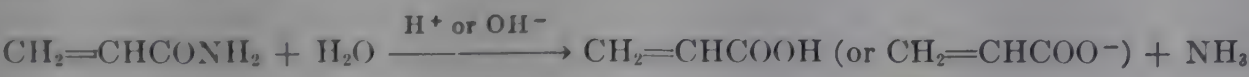
acetone.....	63.1
benzene.....	0.346
chloroform.....	2.66
ethanol.....	86.2
ethyl acetate.....	12.6
<i>n</i> -heptane.....	0.0068
methanol.....	155
water.....	215.5

CHEMICAL PROPERTIES

Acrylamide has relatively good stability when stored in the solid state (1). Solutions of acrylamide may be stabilized by the use of various polymerization inhibitors such as cupric and ferrous salts, *N*-phenyl-2-naphthylamine, cupferron (3), and tetramethylthiuram monosulfide (bis(dimethylthiocarbamoyl)sulfide)(4).

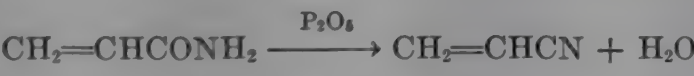
Acrylamide can undergo reactions at the amide group and at the double bond. The ability of the amide group to withdraw electrons facilitates attack by nucleophilic reagents to give 2-carbamoylethyl compounds. Acrylamide is also an active monomer and readily undergoes polymerization and copolymerization reactions.

Reactions of the Amide Group (1). Hydrolysis with either acid or base converts acrylamide to acrylic acid:

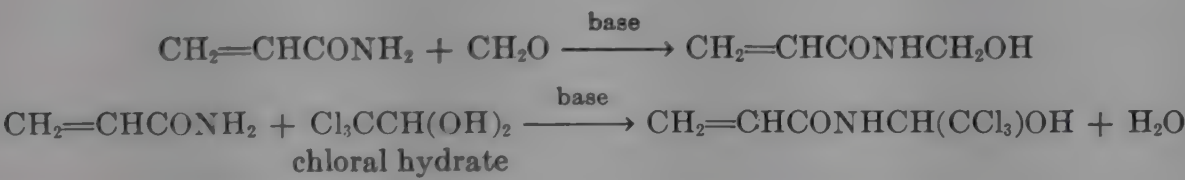


Maximum rate of hydrolysis with sulfuric acid is achieved at an acid concentration between 2.5 and 4.5 molar.

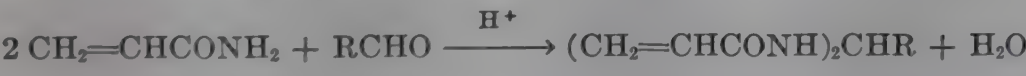
Treatment with a strong dehydrating agent such as phosphorus pentoxide gives acrylonitrile:



Reaction with an aldehyde under basic conditions results in the formation of alcohol:



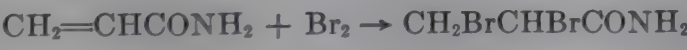
Under acid conditions, *N,N'*-alkylidenebisacrylamides are formed:



These compounds may also be prepared stepwise. This is illustrated for *N,N'*-methylenabisacrylamide:



Reactions of the Double Bond (1). Halogens add to the double bond of acrylamide. This reaction is quantitative in the case of bromine and may be used as a method of analysis:

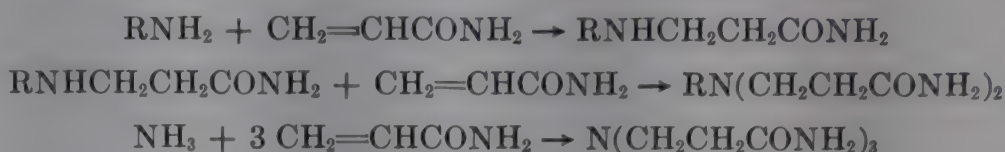


Acrylamide reacts with dienes, such as cyclopentadiene, to give the Diels-Alder addition product:



Addition of nucleophiles to the double bond proceeds easily. Since the reaction introduces the 2-carbamoylethyl group into the substrate, the reaction is often

called carbamoylethylation. Most aliphatic primary and secondary amines as well as ammonia add directly without need of a catalyst:

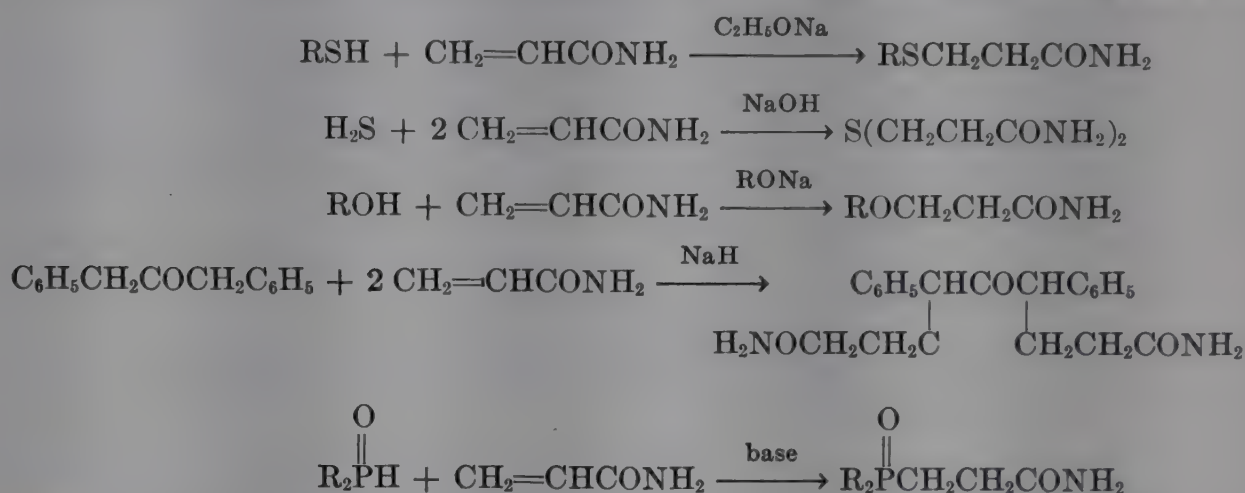


Aromatic amines react in the presence of a catalytic amount of acetic acid:



(when R is an aryl group).

Mercaptans (including hydrogen sulfide), alcohols, ketones, and phosphorus-hydrogen compounds (dialkylphosphine oxides) (5), require a strong base as catalyst:



Dithiocarbamates, being already in the anionic form, react without a catalyst (6):



The reaction of hydrogen halides with acrylamide gives 3-halopropionamides:



With pyridinium chloride, *N*-(2-carbamoylethyl)pyridinium chloride is obtained (7):



Sodium bisulfite adds to give the sodium salt of 3-sulfopropionamide:



The reaction of acrylamide with polymeric hydroxyl-containing materials, such as cellulose (8), starch (9), and poly(vinyl alcohol) (10), proceeds in the presence of a basic catalyst such as NaOH. In the case of cellulose, carbamoylethylation is generally less efficient than cyanoethylation (reaction with acrylonitrile) and only products with low degrees of substitution have been obtained. The amount of reaction can be increased, however, to the point where the product becomes water-soluble when a swelling agent for the cellulose (eg, sodium thiocyanate) is present during reaction (11).

Polymerization. Acrylamide is a versatile, highly reactive monomer which readily undergoes vinyl polymerization to yield a broad spectrum of homopolymers and copolymers of controlled molecular weight and performance characteristics (1).

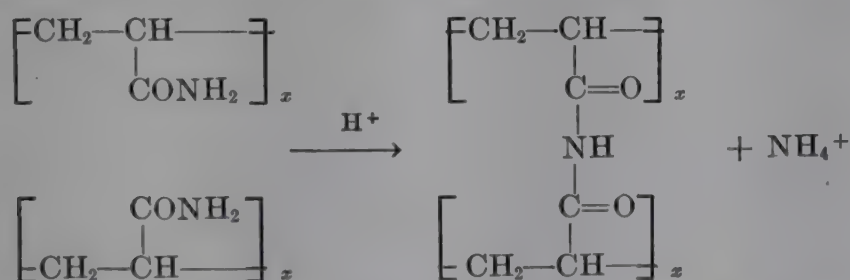
Polyacrylamide is a white odorless solid, soluble in water and insoluble in such solvents as methanol, ethanol, acetone, and hexane. It is slightly soluble in glycerol, ethylene glycol, glacial acetic acid, formamide, and lactic acid. The polymer swells

but does not dissolve in morpholine, propionic acid, propylene glycol, and dimethyl sulfoxide. Polyacrylamide is compatible with most natural and synthetic water-soluble gums, latex systems, salts, and with nonionic, cationic, and anionic surface-active agents (12).

Many of the physical properties and performance characteristics of polyacrylamide are dependent upon its molecular weight. The relationship between the weight average molecular weight, \bar{M}_w , and the intrinsic viscosity, $[\eta]$, for measurements made in 1N NaNO₃ at 30°C is given by the following equation (13):

$$[\eta] = 3.73 \times 10^{-4} (\bar{M}_w)^{0.66}$$

Typical Methods. Acrylamide is readily polymerized in aqueous solution at elevated temperatures with free radical initiators such as *t*-butyl hydroperoxide, hydrogen peroxide, the alkali metal and ammonium persulfates, chlorates, perborates, percarbonates, and the like. Redox catalyst systems are frequently employed for polymerization at lower temperatures, particularly where high-molecular-weight polymers are desired. Redox systems consist of oxidizing agents such as the initiators mentioned above together with reducing agents, such as thiosulfates or bisulfites. A typical redox system is ammonium persulfate and potassium metabisulfite in stoichiometric proportions. Special redox recipes, such as bromate-sulfite, or persulfate-tertiary amine, have been used to achieve very high molecular weights (14). In industrial practice, polymerization is carried out in aqueous solutions of 10–30% concentration at 30–60°C using catalyst concentrations of 0.01–1.0%, based on monomer, at pH 3–6. For polymerization at higher pH values, it is desirable to use special redox systems; combinations of persulfate with amine activators are frequently employed (for example, triethanolamine, *N,N*-dimethyl-1,3-propanediamine, *N,N*-dimethylglycinonitrile, etc). Care should be exercised in polymerizing acrylamide at extreme pH levels. Polymerization at pH 9 or higher is accompanied by hydrolysis of amide groups, while at pH 2.5 or below, imidization may occur which can lead to the formation of crosslinked, relatively insoluble products, as shown below (1):



Acrylamide forms only linear polymers when polymerized at 50°C, but significant amounts of branched polymer result at higher temperatures (such as 78°C (15)).

The water-soluble lower alcohols (methanol, ethanol, and 2-propanol) and the thiols (mercaptosuccinic acid, 2-mercaptoethanol, and mercaptoacetic acid) are used as modifying or chain-transfer agents to control molecular weights. The polymerization is generally conducted in an inert atmosphere of nitrogen or carbon dioxide.

The viscosity increases rapidly during polymerization, and the resulting polymer solution may vary from a clear, viscous syrup to a tough, rubbery mass depending upon the polymer concentration and the molecular weight. Polymerization is usually completed in 3–6 hours and conversions of more than 98% are obtained. If necessary, additional treatment of the polymer solution with ammonia (16) or sulfite (17) may be employed to effect further reduction in residual monomer content. The polymer

solution is then converted to a dry powder by conventional techniques such as drum drying, spray drying, or precipitation in lower alcohols.

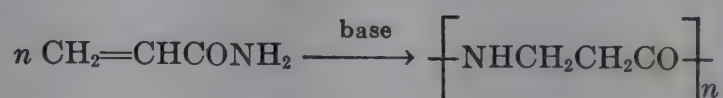
Miscellaneous Methods. Many other polymerization methods have also been employed. In one novel process, small droplets of concentrated aqueous acrylamide solution stabilized by finely divided solids are dispersed and polymerized in an organic solvent, such as xylene (18). In another process, a dispersion of solid acrylamide in an organic solvent is polymerized directly (19).

Polyacrylamides of predetermined molecular weight have been obtained by polymerizing acrylamide in aqueous solutions of lower alcohols. The molecular weight at which the polymer precipitates from solution is controlled by the concentration of alcohol used. 2-Propanol is especially useful for the preparation of low-molecular-weight polymers.

Acrylamide has been polymerized and hydrolyzed in a single continuous operation to yield polymers containing the desired amounts of carboxylate groupings by adding the appropriate quantity of sodium hydroxide to the monomer solution prior to polymerization (20).

A number of recent investigations have dealt with radiation-induced polymerization. Acrylamide was found to polymerize when irradiated with γ rays both in the solid state and in solution. In the solid state, polymerization continues even after irradiation is terminated (21,22). The photopolymerization of acrylamide in aqueous solution can be carried out in the presence of oxygen using combinations of various dyes and reducing agents as sensitizers (23). Free radical initiation is postulated to result from the redox decomposition of hydrogen peroxide by the reducing agent. The hydrogen peroxide is produced by the action of oxygen on the photochemically reduced form of the dye (24).

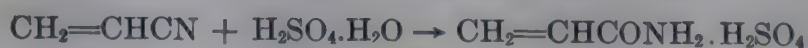
Acrylamide has also been polymerized under anionic conditions in the presence of a free radical polymerization inhibitor to give poly- β -alanine (25).



Manufacture

The methods of preparation of acrylamide may be divided into two groups: those which utilize acrylonitrile as starting material, and miscellaneous other procedures. Historically, the latter were utilized first, but commercially only variations of the acrylonitrile process have been important.

From Acrylonitrile. Acrylonitrile (qv) is particularly suitable as starting material because of its low cost and ready conversion to acrylamide sulfate by the use of sulfuric acid, at the concentration corresponding to its monohydrate:



The hydration is conveniently carried out by adding acrylonitrile slowly to the acid. The reaction is strongly exothermic and is complete in about an hour at 90–100°C (2) or in 5–8 minutes at 155–175°C (26). It is necessary to use a polymerization inhibitor which is not affected by the strongly acid conditions prevailing. Copper and iron salts are particularly useful for this purpose. If iron salts are used, they can be removed from acrylamide with inorganic phosphates (27).

Although the preparation of acrylamide sulfate offers no great difficulties, isolation of the pure acrylamide is complex. Dilution of acrylamide sulfate with water

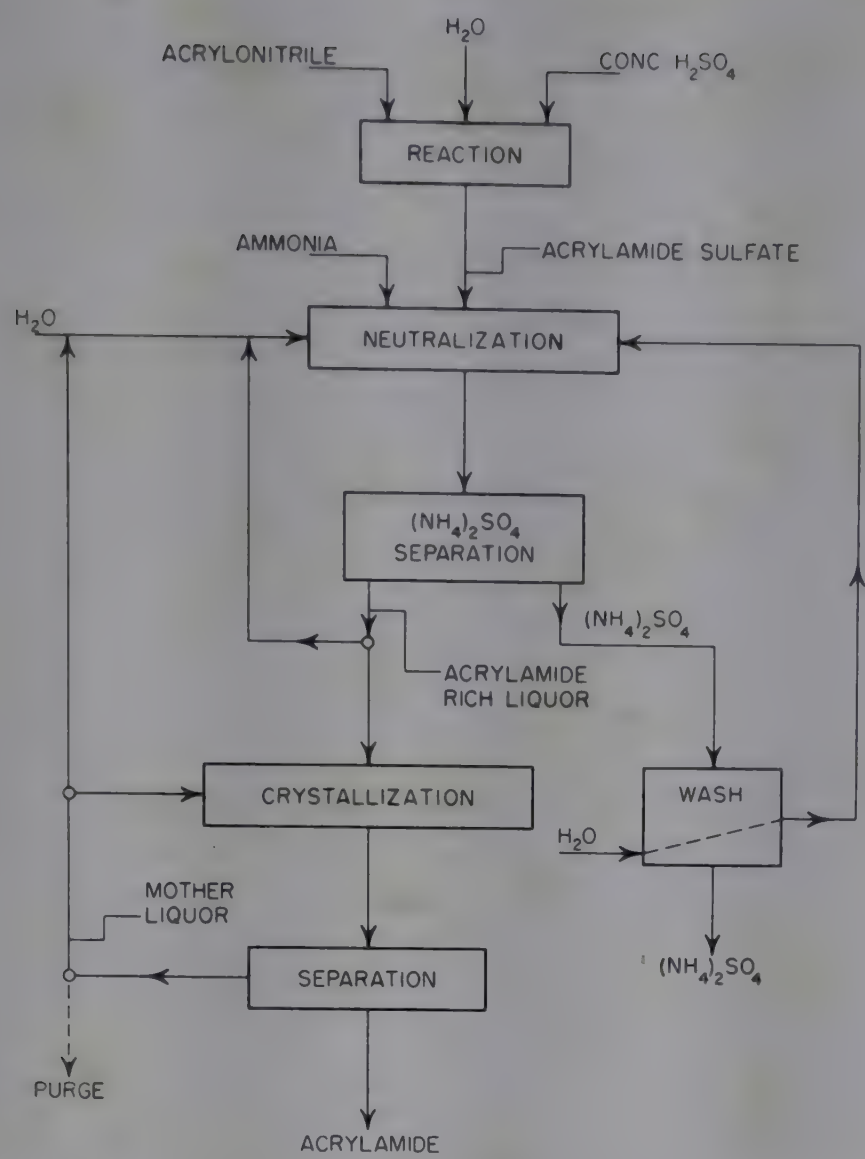


Fig. 1. Flowsheet for production of acrylamide.

yields acrylamide and sulfuric acid, but it also tends to cause hydrolysis. Consequently, it is desirable to neutralize the acid; but the separation of the resulting salt from the acrylamide is complicated by the very high solubility of the amide in water and its tendency to polymerize. Furthermore, some bases, such as ammonia (see under Reactions of the double bond), can react with acrylamide to produce undesirable by-products. The numerous processes which have been proposed overcome these difficulties with varying degrees of success.

Most practical methods of isolating acrylamide involve neutralization in water of the sulfuric acid to give a water-insoluble salt. The salt is then removed by filtration and the filtrate is concentrated and/or cooled to recover crystals of acrylamide.

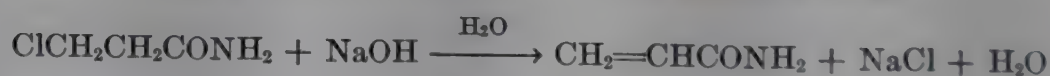
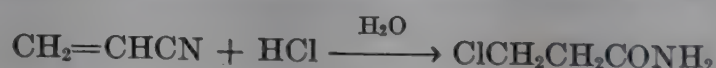
Suitable bases are not only lime, which gives insoluble calcium sulfate, but surprisingly, also ammonia (28) and the alkali metal hydroxides and carbonates (29). According to refs. 28 and 29, ammonia and alkali metal hydroxides and carbonates may be used, because ammonium, sodium, and potassium sulfate have very low solubilities in concentrated solutions of acrylamide (< 1 g per 100 g of saturated solution of acrylamide at 50°C) and the solubilities *decrease* with increasing temperatures. The neutralization may, therefore, be conducted in a concentrated solution of acrylamide at a temperature of about 50°C. The sulfate is removed by filtration; upon cooling the filtrate, acrylamide containing only minor amounts of salt crystallizes. The mother

liquor may be recycled to serve as the medium for further neutralization of acrylamide sulfate, particularly in a continuous operation. Some additional acrylamide may be obtained by washing the salt. A flowsheet for such a process is given in Figure 1 (30).

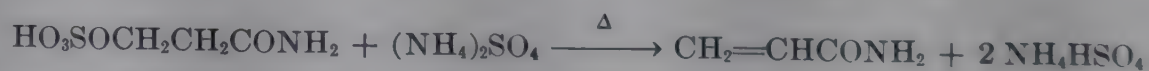
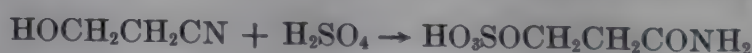
Other methods of separating the salt make use of extraction of acrylamide with an organic solvent or of vacuum distillation or sublimation of the amide (2). These methods are not believed to be in commercial use.

A method for the direct separation of the acrylamide from the sulfuric acid which does not require neutralization has been patented (31). In this process, acrylamide sulfate is diluted with water and the solution is passed through a column of cation-exchange resin. Successive fractions of the effluent contain sulfuric acid, a mixture of acrylamide and acrylic acid, and finally acrylamide. The use of water to elute the product from the resin not only dilutes the acrylamide, but also results in a significant amount of hydrolysis to acrylic acid. The separation of the various fractions is not always complete and some sulfuric acid tends to contaminate the acrylamide. This acid must be neutralized before it causes further hydrolysis. The cation-exchange resin is typically a sulfonated copolymer of approximately 90% styrene, 6% ethylvinylbenzene, and 4% divinylbenzene. It may be used either in the acid form, as described above, or in the salt form. In the latter case, less hydrolysis of acrylamide is likely to take place and the effluent will contain a sulfate salt, such as ammonium hydrogen sulfate. This variation is, therefore, tantamount to a neutralization of the sulfuric acid with the resin. The dilute aqueous solutions of acrylamide obtained may be concentrated by removal of the water by evaporation, spray drying (32), or azeotropic distillation (33).

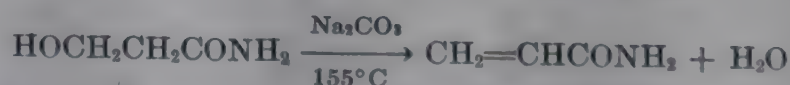
The use of aqueous hydrochloric acid has been suggested as a substitute for sulfuric acid in the reaction with acrylonitrile. The product of the reaction is 3-chloropropionamide which, upon treatment with an alkali, yields acrylamide (34).



Ethylene cyanohydrin, $\text{HOCH}_2\text{CH}_2\text{CN}$, an intermediate in the manufacture of acrylonitrile from ethylene oxide, may be substituted for acrylonitrile as the starting material. Treatment with 100% sulfuric acid gives a compound described as the sulfate of 3-hydroxypropionamide. Upon treatment with ammonium sulfate, acrylamide can be distilled off at a temperature of 140–165°C under reduced pressure (35):



Alternatively, 3-hydroxypropionamide could be isolated after treatment with sulfuric acid and subjected to catalytic dehydration at 155°C (2):



Lactonitrile, the 2-hydroxypropionitrile, could not be converted to acrylamide by similar methods (2).

Miscellaneous Methods (2). Most of the methods under this heading have been described primarily in the patent literature; none are believed to be in commercial usage.

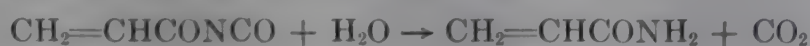
The first reported preparation of acrylamide was carried out by the reaction of acryloyl chloride with dry ammonia in benzene:



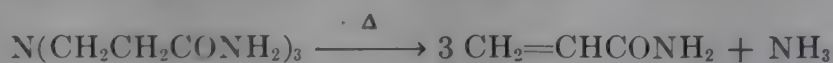
Similarly, acrylic anhydride has been used:



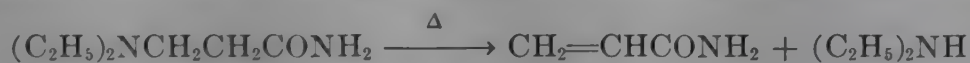
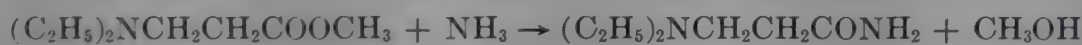
Acryloyl isocyanate reacts with water to give the amide:



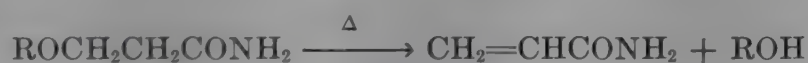
Esters of acrylic acid may be converted to 3-aminopropionamides which, upon pyrolysis, yield acrylamide. Methyl acrylate was thus converted with ammonia to the 3,3,'3"-nitrilotrispropionamide which upon heating to 208–230°C at 15 mm gave acrylamide (36):



Similarly amines may be used, but these require an additional processing step. This is illustrated for diethylamine:



3-Alkoxypropionamides also yield acrylamide upon pyrolysis:



Suitable catalysts are lithium phosphate, titania, volatile strong mineral acids, and calcium oxide (2,37,38). The 3-alkoxypropionamides may be prepared by base-catalyzed addition of alcohols to acrylate esters, followed by reaction with ammonia:



or, preferably, by base-catalyzed addition of alcohols to acrylamide. Obviously, this latter procedure is not suitable as a method of manufacture for acrylamide.

The reaction of acetylene, carbon monoxide, and amines is an excellent method of preparing *N*-substituted acrylamides:



The same reaction has been described to yield the parent compound when ammonia is used instead of an amine. But this claim could not be confirmed by other investigators (2).

Economic Aspects

Although acrylamide was first prepared in 1893, it was not until acrylonitrile became available commercially in 1940 that interest was shown in its preparation and properties. It was offered to the trade in development quantities by the American Cyanamid Company in 1952, and commercial production began in 1954. Acrylamide

production is presently in the multimillion pound category and the price was reduced in 1961 from \$0.58 to \$0.52 per pound.

Specifications and Analysis

Typical commercial specifications for acrylamide are as follows:

appearance.....	white free-flowing crystals
assay.....	98% minimum
water.....	0.8% maximum
total iron, as Fe.....	0.0015% maximum
color of 20% solution (APHA scale).....	50 maximum
water insolubles.....	0.02% maximum
butanol insolubles.....	1.5% maximum

Further purification may be achieved by sublimation or by recrystallization from acetone or ethyl acetate.

Acrylamide is assayed by a modification of the standard iodine determination for unsaturation (1). The weighed sample of acrylamide is allowed to react with a standard 0.1N KBrO₃-KBr reagent in the presence of sulfuric acid. Potassium iodide is then added, and the solution is titrated with standard thiosulfate solution, using starch as indicator.

Small amounts of acrylamide in polymers may be determined by polarographic reduction. The half-wave potential in a 1.0M solution of tetramethylammonium hydroxide at 30°C is -1.7 volts with a mercury anode.

Toxicity

In experimental animals, repeated ingestion or absorption of acrylamide produces characteristic toxic effects on the central nervous system. Signs of poisoning include general muscular weakness, ataxia, and, in extreme cases, loss of control of the hind-quarters. These signs are slowly reversible following termination of exposure, provided the degree of poisoning has not been severe. The animal studies indicate that acrylamide is absorbed through the unbroken skin, and that it is a mild primary skin irritant and eye irritant.

Health experience in the manufacture and use of acrylamide has been good. This circumstance may be the result of either the maintenance of strict hygienic precautions, or the possibility that humans are less susceptible to the product. However, all hygienic measures must be based on the assumption that humans are equally susceptible. Skin contact with the solid or solutions, inhalation of dust, or inadvertent ingestion must be prevented.

Toxicological investigations with polyacrylamide indicate a very low order of toxicity. Except to the extent that it contains residual monomer, polyacrylamide exhibits no neurotoxic action. It is not expected to be injurious to health under normal circumstances of industrial handling.

Uses

The utility of acrylamide resides primarily in its ability to be converted to useful polymers. Polyacrylamide is a very effective flocculant for finely divided solids in

aqueous suspensions. It may be used in acid, neutral, or alkaline systems even in the presence of high concentrations of electrolytes. It has found wide application in the treatment of ores, particularly acid-leached uranium ore, mineral and metal particles, sewage, industrial wastes, and chemical precipitates. Polyacrylamide is usually fed as very dilute solutions which cause rapid agglomeration and sedimentation. Extremely high-molecular-weight polyacrylamides (approximately 20 million) have been found to be exceptionally effective flocculants (39).

Mixtures of acrylamide with small proportions of *N,N'*-methylenebisacrylamide have been finding increasing application as chemical grouts. They are available commercially under the trademark "AM-9" (40). Aqueous solutions of the monomers together with a redox catalyst are injected into soil formations. In a predetermined period of time, which may be controlled, the monomers polymerize giving a cross-linked rigid gel which prevents the passage of water through the mass and also binds the soil particles together. AM-9 has been used to seal off the flow of water into oil wells, drill holes, basements, tunnels, mine shafts, caissons, and dams. For normal use, the catalyst is composed of 3-dimethylaminopropionitrile and ammonium persulfate. The gel time is controlled primarily by the catalyst concentration (40).

Copolymers of acrylamide and acrylic acid are being used as stock additives for improving the dry strength of paper (41). The increase is obtained with little change in bulk or porosity. This property is particularly useful in the manufacture of printing papers. The polymers are usually added in amounts corresponding to 0.25–0.75% of the weight of the dry fiber. For optimum results, the pH should be between 4.0 and 5.0 and alum should be present. High-molecular-weight acrylamide copolymers have also shown considerable promise for increasing the retention of mineral fillers in papermaking. Improvement in drainage rate and wet web strength have also been obtained.

Copolymers of acrylamide and acrylic acid have been found to control the loss of fluid from oil well cements in hydraulic cementing operations (42). Polyacrylamide of high molecular weight has been claimed to be useful as a thickening agent for water used in a secondary oil recovery method called water flooding. The thickened water is used to drive oil through the formation to a producing well (14). Interpolymers of acrylamide and other monomers, such as vinyl acetate, ethyl acrylate, methyl methacrylate, styrene, etc, form the base for a group of commercially important surface coatings (43–45).

The use of acrylamide in applications other than those involving polymers has not achieved prominence. The reaction with polyhydroxy compounds has already been cited above. A recent communication describes a new series of antitumor agents which are derivatives of acrylamide; *N*-[(3-bromopropionamido)methyl]acrylamide, $\text{CH}_2=\text{CHCONHCH}_2\text{NHCOCH}_2\text{CH}_2\text{Br}$, was particularly effective (46). Many other applications have been described, particularly in the patent literature, but few are believed to be in actual commercial usage and none consume substantial quantities of acrylamide at the present time.

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40. *AM-9 Chemical Grout*, American Cyanamid Company, New York, 1960.
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44. U.S. Pats. 2,919,254 (1959), 2,940,943 and 2,940,944 (1960), R. M. Christenson and H. A. Vogel (to Pittsburgh Plate Glass).
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ACRYLIC ACID AND DERIVATIVES

Historically, the acrylics, a term which includes derivatives of acrylic acid ($\text{CH}_2=\text{CHCOOH}$) and of methacrylic acid ($\text{CH}_2=\text{C}(\text{CH}_3)\text{COOH}$), achieved importance with the development of useful and versatile polymeric materials in the 1930s. This followed the original polymerization of acrylic esters in 1873 by Caspray and Tollens and the discovery of acrylic plastics in 1901 by Otto Röhm (1). Applications which have unfolded for the acrylic family include plastic sheet and molding powder for signs, construction units, and decorative emblems and insignia; polymer solutions for coatings applications; emulsion polymers for water-based paint formulations, leather finishing, and paper coating; and a variety of polymers for sizing, treating, and finishing textiles. Derivatives of both acrylic acid and methacrylic acid are used, and many applications require the use of both types in order to achieve desired properties. In many respects, the chemistry of acrylic acid and methacrylic acid derivatives is the same, but there are important differences in certain properties of derived materials. For a discussion of methacrylic acid and its derivatives, see Methacrylic compounds.

Included in this article are the following acrylic acid monomers and their derived polymers:

Compound	Formula	Molecular weight
acrylic acid (ethenecarboxylic acid)	$\text{CH}_2=\text{CHCOOH}$	72
acrylic anhydride	$\text{CH}_2=\text{CHCOOOCCH}=\text{CH}_2$	126
acryloyl chloride	$\text{CH}_2=\text{CHCOCl}$	90.5
sodium acrylate	$\text{CH}_2=\text{CHCOONa}$	94
acrylamide	$\text{CH}_2=\text{CHCONH}_2$	71
methyl acrylate (and other acrylic acid esters)	$\text{CH}_2=\text{CHCOOCH}_3$	86

Physical Properties

Tables 1 and 2 list certain properties for acrylic acid and some of its representative derivatives. The physical properties of the acrylic acid esters are listed in Table 3.

Table 1. Physical Properties of Some Acrylic Acid Monomers

Property	Acrylic acid	Acrylic anhydride	Acryloyl chloride	Acrylamide	Methyl acrylate
melting point, °C	13.5			84.5	−75
boiling point, °C/mm Hg	141/760	38/2	75/760	125/25	80/760
density, g/ml	1.045 (25°C)		1.1127 (20°C)	1.122 (30°C)	0.949 (25°C)
refractive index, n_D^{20}	1.485 (25°C)	1.4487	1.4337		
flash point (COC), °F	155				60
kinematic viscosity, cks, at 25°C	1.1				
dissociation constant	5.50×10^{-5}				
pK _B	4.26				

Representative acrylic monomers are listed in Table 2 with indication of solubility, ie, above five grams per 100 grams of solvent, at room temperature in a variety of solvents.

Table 2. Solubility Data for Some Acrylic Monomers^a

Solvent	Acrylic acid	Acrylamide	Sodium acrylate	Methyl acrylate
water	S	S	S	I ^b
methanol	S	S	I	S
ether	S		I	S
Cellosolve	S	S	I	S
acetone	S	S	I	S
ethyl acetate	S	S	I	S
chloroform	S	I ^b	I	S
benzene	S	I	I	S
hexane	S	I	I	I
dimethylformamide	S		I	S

^a Solubility above 5 g/100 g solvent at room temperature.

^b Soluble to the extent of 4–5 g/100 g solvent.

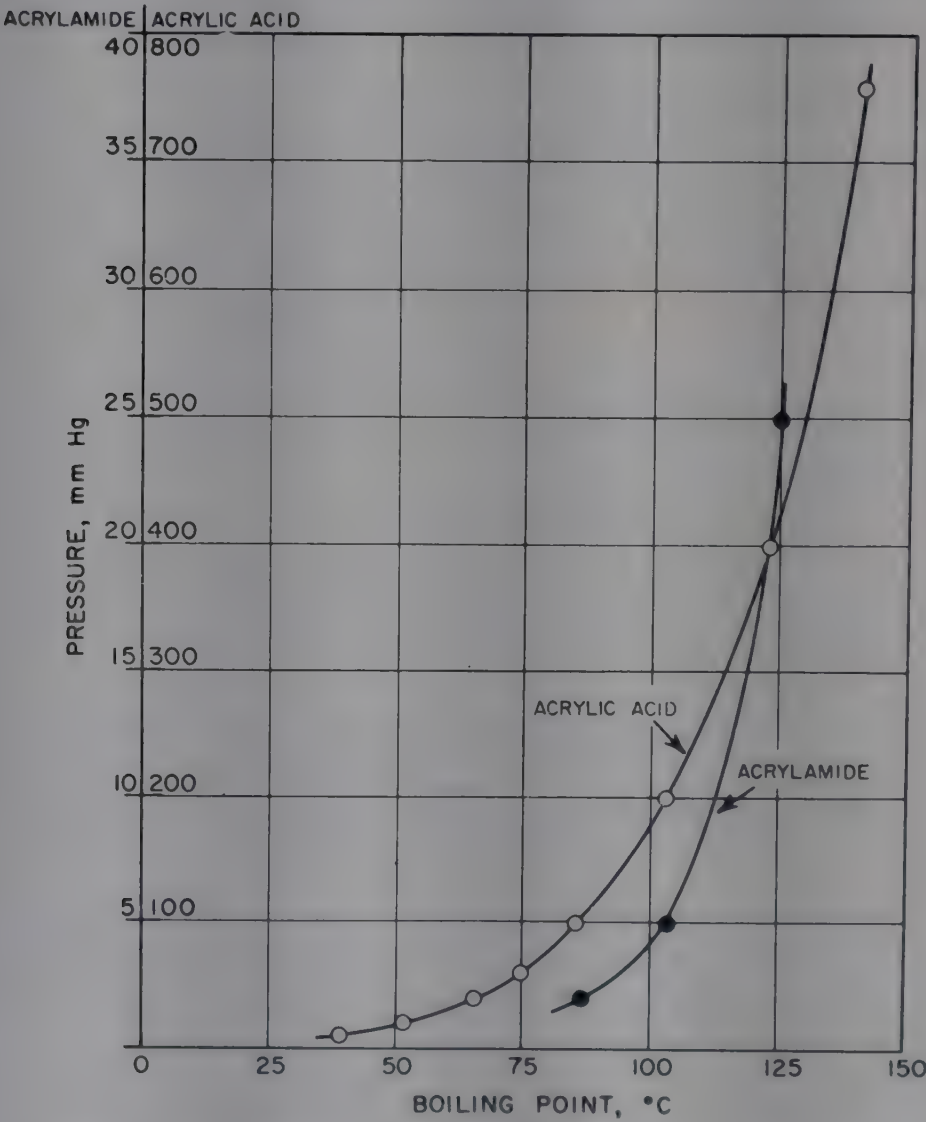


Fig. 1. Ebulliometric data for acrylic acid and acrylamide.

A graph of the boiling points of acrylic acid and of acrylamide as a function of pressure is shown in Figure 1. The variation of vapor pressure of certain acrylic esters as a function of temperature is shown in Figure 2.

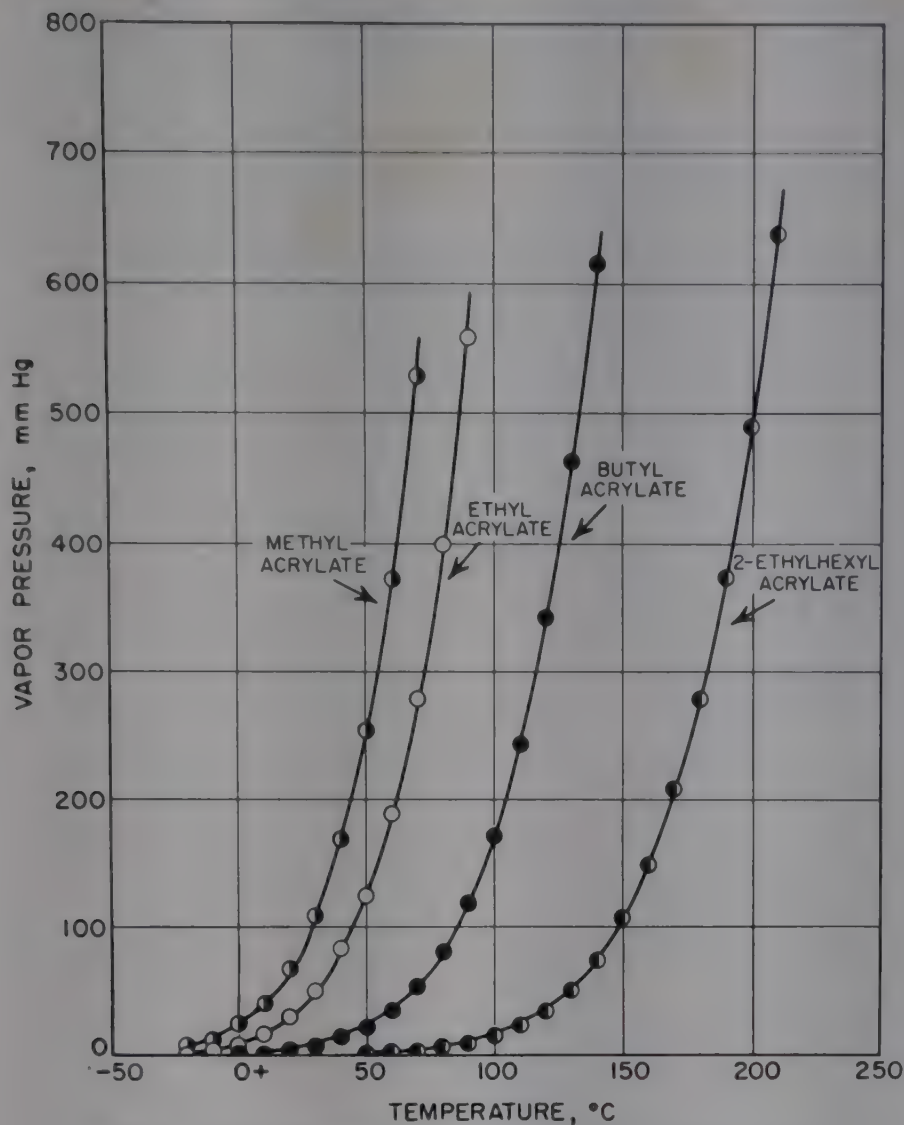


Fig. 2. Vapor pressure data for esters of acrylic acid.

Table 3. Physical Properties of Acrylic Esters, CH₂=CHCOOR

R	Boiling point		n_D^{20}	d_4^{20}
	°C	mm Hg		
<i>n-Alkyl esters (2)</i>				
methyl	80	760	1.4040	0.9535
ethyl	43	103	1.4068	0.9234
propyl	44	40	1.4130	0.9078
butyl	35	8	1.4190	0.8998
pentyl	48	7	1.4240	0.8920
hexyl	40	1.1	1.4280	0.8882
heptyl	57	1	1.4311	0.8846
octyl	57	0.05	1.4350	0.8810
nonyl	76	0.2	1.4375	0.8785
decyl	120	5	1.4400	0.8781
dodecyl	120	0.8	1.4440	0.8727
tetradecyl	138	0.4	1.4468	0.8700
hexadecyl	170	1.5	1.4470 (30°C)	0.8620 (30°C)
<i>Secondary and branched chain alkyl esters (3)</i>				
isopropyl	52	103	1.4060	0.8932
isobutyl	62	50	1.4150	0.8896
sec-butyl	60	50	1.4140	0.8914

(continued)

Table 3 (continued)

R	Boiling point		n_D^{20}	d_4^{20}
	°C	mm Hg		
2-methylbutyl	45	10	1.4220	0.8871
3-methylbutyl	43	7	1.4230	0.8911
1-ethylpropyl	63	27	1.4210	0.8883
2-methylpentyl	88	32	1.4282	0.8850
2-ethylbutyl	80	20	1.4292	0.8912
1,3-dimethylbutyl	71	29	1.4220	0.8723
1-methylhexyl	66	5.7	1.4282	0.8750
2-ethylhexyl	85	8	1.4365	0.8852
1-methylheptyl	79	5.4	1.4312	0.8754
4-ethyl-1-methyloctyl	94	2.2	1.4415	0.8758
4-ethyl-1-isobutyloctyl	96	0.3	1.4448	0.8685
<i>Esters of olefinic alcohols (4)</i>				
allyl	47	40	1.4320	0.9441
2-methylallyl	68	50	1.4372	0.9285
1-methylallyl	70	97	1.4299	0.9066
2-butenyl	60	23	1.4422	0.9344
2-chloroallyl	72	29	1.4600	1.1243
3-chloroallyl	87	34	1.4680	1.1385
1,3-dimethyl-3-butenyl	62	14	1.4380	0.9027
3,7-dimethyl-7-octenyl	108	5.4	1.4500	0.8879
3,7-dimethyl-2,6-octadienyl	116	6.2	1.4690	0.9121
3,7-dimethyl-6-octenyl	107	4.2	1.4591	0.9026
cinnamyl	108	1.2	1.5508 (25°C)	1.0495 (25°C)
furfuryl	93	16	1.4800	1.1125
<i>Aminoalkyl esters (5)</i>				
2-(dimethylamino)ethyl	61	11	0.9434	1.4375
2-(diethylamino)ethyl	70	5	0.9251	1.4425
2-(dibutylamino)ethyl	82	0.3	0.8977	1.4460
3-(diethylamino)propyl	44	0.1	0.9180	1.4441
2-(dibutylamino)propyl	77	0.2	0.8880	1.4440
3-(dibutylamino)propyl	83	0.2	0.8952	1.4480
2-morpholinoethyl	67	0.2	1.0711	1.4728
2-[N-(2-hydroxyethyl)ethylamino]-ethyl	77	0.2	1.0211	1.4662
<i>Esters of ether alcohols (6)</i>				
2-methoxyethyl	59	12	1.4272	1.0131
2-ethoxyethyl	78	23	1.4282	0.9819
2-(2-chloroethoxy)ethyl	74	0.8	1.4580	1.1471
2-isopropoxyethyl	82	19	1.4258	0.9549
2-butoxyethyl	64	2	1.4323	0.9497
2-(2-ethylhexoxy)ethyl	87	0.5	1.4408	0.9215
2-phenoxyethyl	84	0.2	1.5200	1.1037
2-benzyloxyethyl	118	2.3	1.5075	1.0741
2-(<i>p</i> -tert-butylphenoxy)ethyl	117	0.1	1.5093	1.0326
2-(2,4-di-tert-pentylphenoxy)ethyl	165	0.8	1.4905 (54°C)	0.9612 (54°C)
2-(2-methoxyethoxy)ethyl	86	4.6	1.4392	1.0421
2-(2-ethoxyethoxy)ethyl	45	0.15	1.4390	1.0145
2-(2-butoxyethoxy)ethyl	103	2.3	1.4394	0.9821
2-(2-phenoxyethoxy)ethyl	118	0.3	1.5108	1.1103
tetrahydrofurfuryl	87	0.9	1.4580	1.0643
4-methoxybenzyl	100	0.1	1.5260	1.1061

Table 3 (continued)

R	Boiling point		n_D^{20}	d_4^{20}
	°C	mm Hg		
<i>Cycloalkyl esters (7)</i>				
cyclohexyl	75	11	1.4600	0.9796
2-methylcyclohexyl	69	5	1.4560	0.9546
3-methylcyclohexyl	74	6	1.4550	0.9541
4-methylcyclohexyl	55	2	1.4550	0.9537
3,3,5-trimethylcyclohexyl ^a	72	2	1.4542	0.9292
3,3,5-trimethylcyclohexyl ^b	40	0.2	1.4560	0.9346
4- <i>tert</i> -pentylcyclohexyl	95	1	1.4705	0.9490
4-cyclohexylcyclohexyl ^c	115	1	1.4810 (50°C)	0.9500 (50°C)
hydroabietyl	177	0.3	1.5172	1.0181
<i>Esters of halogenated alcohols (8-10)</i>				
2-bromoethyl	53	5	1.4770	1.4774
2-chloroethyl	74	29	1.4477	
3-bromopropyl	96	18	1.4786	1.4106
2,3-dibromopropyl	105	6	1.5220	1.7803
1-bromoisopropyl	69	10	1.4712	1.3885
3-chloropropyl	79	14	1.4522	1.1122
2,3-dichloropropyl	58	0.5	1.4765	1.2603
1,3-dichloroisopropyl	50	1	1.4725	1.2592
1,1-dihydroperfluoro-ethyl	46	125	1.3480 (25°C)	1.216 (25°C)
-propyl	50	100	1.3363	1.32
-butyl	51	50	1.3317	1.409
-pentyl	57.5	30	1.3289 (25°C)	1.48 (25°C)
-hexyl	63.5	20	1.3296	1.54
-octyl	55	2.5	1.3289	1.63
-decyl	53	0.03	1.3279	1.689
<i>Nitroalkyl esters (11,12)</i>				
2-nitroethyl	100	5	1.4510	1.204
2-nitropropyl	92	4	1.4448	1.143
2-nitrobutyl	102	6	1.4452	1.112
2-methyl-2-nitropropyl	102	8	1.4455	1.112
2,2-dinitropropyl	71	0.4	1.4610	
2,2-dinitrobutyl	95	1	1.4570	
3,3-dinitrobutyl			1.4660	
2,2-dinitropentyl	73	0.008	1.4571	
<i>Glycol diacrylates (13)</i>				
ethylene glycol (monoester)	40	0.01	1.4482 (25°C)	
ethylene glycol	70	1	1.4529	
propylene glycol	63	0.3	1.4470	
1,3-propanediol	65	<1	1.4529	
1,4-butanediol	83	0.3	1.4538	
diethylene glycol	94	0.2	1.4572	
1,5-pentanediol	94	0.3	1.4551	
triethylene glycol	125	0.2	1.4609	
dipropylene glycol	95	0.3	1.4488	
2,5-hexanediol	85	0.2	1.4496	
2,2-diethyl-1,3-propanediol	90	0.1	1.4589	
2-ethyl-1,3-hexanediol	106	0.8	1.4542	
1,10-decanediol	145	0.1		

^a Melting point, 35°C.

^b Melting point, 51°C.

^c Melting point, 41°C.

Chemical Reactions

Chemical reactions of acrylic acid and its derivatives may be divided into two main groups: reactions that take place at the functional group; and reactions that involve the double bond (14).

Functional Group Reactions. All reactions of the functional group of the acrylic acid series are predicated upon proper control of conditions to prevent the major reaction of the double bond, that is, polymerization. This is conveniently accomplished by the use of appropriate polymerization inhibitors and by the use of a reaction temperature as low as practical. In general, the same types of functional group reactions can be carried out on the polymers as on the monomers if it is remembered that carrying such reactions to completion becomes progressively more difficult as the molecular weight of the specific polymer becomes higher, and that markedly different polymers with rings, side chains, and crosslinking bridges may be produced by intra- and interpolymer reactions, especially in the case of copolymers.

Acrylic acid may be converted to the following compounds:

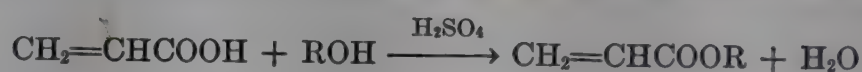
a. Salts, by the action of a suitable base in aqueous medium. The salts produced are much more highly ionized than the acid; this has produced some interesting results in both polymer preparation and properties (15). Salts may also be prepared by the saponification of acrylonitrile and acrylic esters.

b. Acrylic anhydride, (1) by treatment with acetic anhydride, (2) by treating sodium acrylate with acryloyl chloride, and (3) by the semicatalytic reaction of acetylene with carbon monoxide and water (see p. 295).

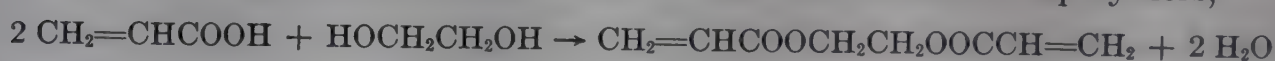
c. Acryloyl chloride, by reaction with phosphorus oxychloride or thionyl chloride.

d. Esters, by reaction with

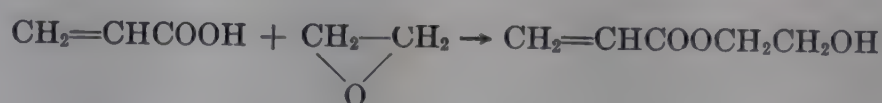
(1) alcohols under catalytic conditions at elevated temperatures,



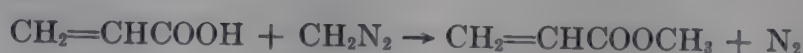
(2) dihydric alcohols to provide multifunctional polymerization agents for use in crosslinking polymers to achieve less soluble and insoluble copolymers,



(3) ethylene oxide (or other alkylene oxide), with appropriate precautions to prevent the formation of ethylene bisacrylate, unless this is the desired product,



(4) diazomethane. This reaction is particularly effective with polymeric acids (16).



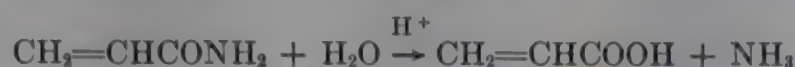
e. Amides, by reaction with ammonia or primary or secondary amines.

Acrylic anhydride may be readily hydrolyzed to produce two moles of acrylic acid or it may be saponified to produce the corresponding salt. Esterification may also be conducted with alcohols and alkylene oxides.

Acryloyl chloride may be treated as follows: hydrolyzed to form acrylic acid; esterified by reaction with an alcohol; and converted to acrylic anhydride by reaction with sodium acrylate, or to a mixed anhydride with other sodium salts.

Acrylamide may be converted (17) to the following compounds:

a. Acrylic acid, by controlled hydrolysis with an appropriate inorganic acid present.



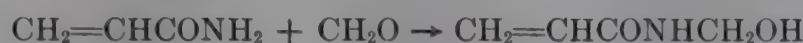
b. Acrylates, by reaction in aqueous medium with suitable bases.



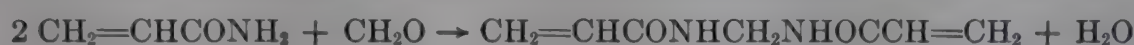
c. An acrylic ester, by reaction with an alcohol and sulfuric acid.



d. *N*-Hydroxymethylacrylamide, by controlled reaction with one mole of formaldehyde.



e. *N,N'*-Methylenebisacrylamide, by further reaction with formaldehyde.

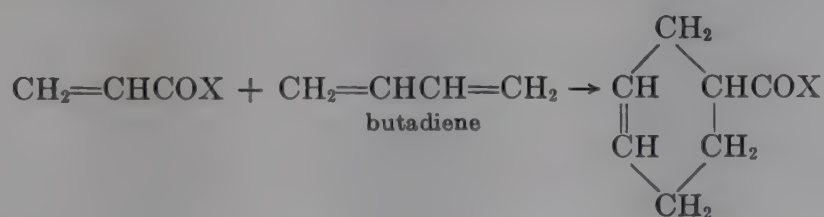


Esters of acrylic acid may be readily converted as follows: to salts by saponification with the appropriate base; to other esters, preferably of higher alcohols, by ester-interchange with azeotropic removal of the lower-boiling alcohol and thus forcing the reaction toward completion; and to amides by aminolysis.

Unsaturated Group Reactions. For the purpose of illustrating the reactions of acrylic acid and its derivatives involving the double bond, these monomers may be represented generically by the formula $\text{CH}_2=\text{CHCOX}$, where X is OH, Cl, ONa, or OR, in which R is an alkyl group. A comprehensive review of the literature through 1952 of these reactions is given by Riddle (14).

Polymerization. This is by far the most important reaction of the acrylic acid series and will be discussed in some detail on p. 303.

Diels-Alder reactions. Substituted ring compounds are formed readily.



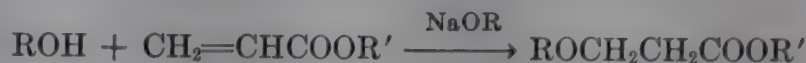
Addition of Halogens. Bromine adds quantitatively to acrylic esters at room temperature and below to form 2,3-dibromopropionic esters. Prior to the advent of gas chromatography, this reaction provided the basis for the determination of the purity of acrylic esters. Likewise, the addition of chlorine to acrylic esters takes place essentially quantitatively at normal temperatures when carried out in the presence of small amounts of dimethylformamide (18).

Addition of Halogen Acids. Addition of hydrogen bromide and hydrogen chloride to acrylic esters occurs at 0–25°C with essentially quantitative yields of the 3-halopropionic esters (19).



Addition of Hydrogen Cyanide. Hydrogen cyanide may be added to acrylic esters to produce the 3-cyano derivative.

Addition of Alcohols. Primary and secondary (but not tertiary) alcohols add readily to acrylic esters, in the presence of strongly basic catalysts, to give 3-alkoxypropionates (20).



If R and R' are not identical, ester interchange may occur simultaneously, with a resultant mixture of products.

Acrylamide may be converted to 3-alkoxypropionamides by reaction with an alcohol in the presence of a catalyst such as sodium ethoxide.



Addition of Sulfur Compounds. Hydrogen sulfide reacts with two moles of methyl acrylate, in the presence of alkaline catalysts, to give high yields of dimethyl 3,3'-thiodipropionate (21,22).



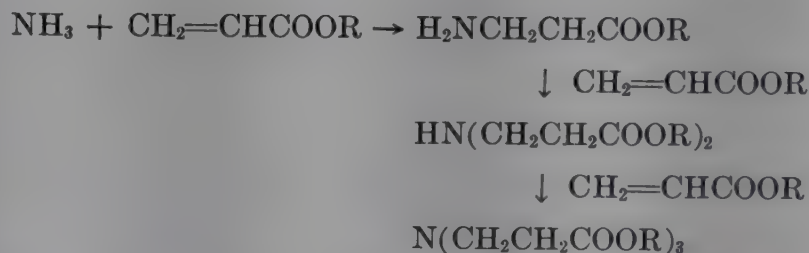
Mercaptans add very readily to acrylic esters in the presence of alkaline catalysts to give excellent yields of 3-alkyl (or aryl) thiopropionates (23). The reaction is often quantitative at room temperature.



Acrylamide and acrylic esters may be converted to a 3-sulfo derivative, sodium salt, by reaction with sodium hydrogen sulfite.

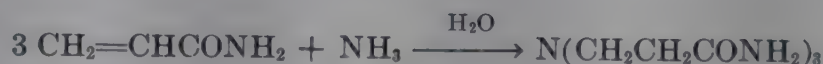


Addition of Ammonia and Amines. Addition of ammonia to acrylic esters results first in the formation of a β -alanine ester, followed by reaction with a second and third mole of acrylic ester.

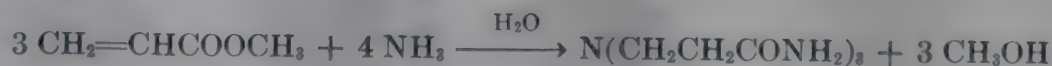


These reactions have been shown to be reversible (24). By use of appropriate conditions of temperature and pressure and by recycling of residues from a previous batch, it is possible to obtain 70% yields of the β -alanine ester (25).

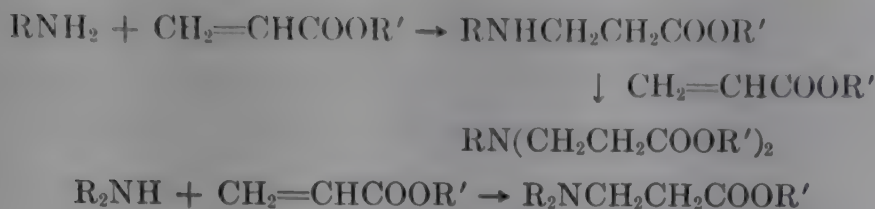
Similarly, acrylamide may be converted to tris(2-carbamoyl)ethylamine by reaction with ammonia and water.



With dilute aqueous ammonia and acrylic esters, ammonolysis of the tertiary amino ester, $\text{N}(\text{CH}_2\text{CH}_2\text{COOR})_3$, results with yields up to 90% of the corresponding amide (26).



In a manner similar to that of ammonia, primary and secondary amines add to acrylic esters to form substituted 3-aminopropionates.

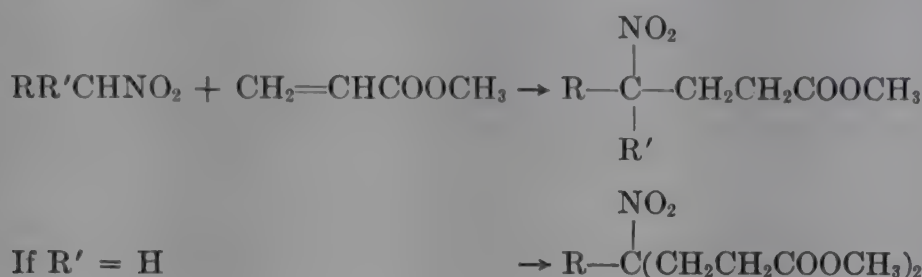


Further reaction of the amine may occur to convert the ester group to the corresponding amide group. Reaction conditions and yield data for the reactions of a large number of aliphatic, aromatic, and heterocyclic amines have been summarized by Riddle (14).

Acrylamide reacts with a secondary amine to give a 3-alkylaminopropionamide.



Addition of Nitroparaffins. Nitroparaffins add readily to acrylic esters, in the presence of alkaline catalysts, to give 4-nitroesters (27,28).



Preparation and Manufacture

The techniques for preparing acrylic acid and each of its major derivatives will be considered in order. The preparative methods are presented in an approximate order of their commercial practicality, based on current knowledge, with the most feasible methods given first.

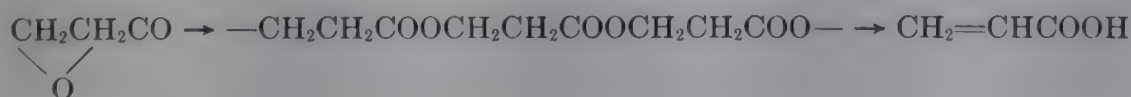
ACRYLIC ACID

Ethylene Cyanohydrin Method. This process involves the acidic hydrolysis and dehydration of ethylene cyanohydrin (from ethylene oxide and hydrogen cyanide) and the removal of the product from the reaction mixture by distillation. Like all other preparations of polymerizable monomers, care must be exercised to remove the product from the reaction mixture and either inhibit or appropriately cool it before uncontrolled polymerization can ensue (29).



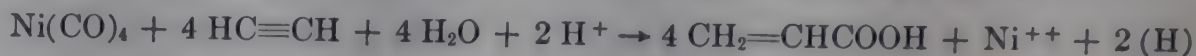
It is not intended to suggest that hydrolysis takes place before dehydration, or vice versa. It is likely that the two reactions are essentially simultaneous.

β -Propiolactone Method. This commercial method is based on the polymerization of β -propiolactone and the destructive distillation of this polymer to form acrylic acid (30).

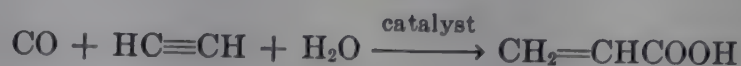


Carbonyl Reaction. Basic raw materials in the preparation of acrylic acid by the carbonyl reaction are acetylene, carbon monoxide (supplied as such or in the form of nickel carbonyl), and water. Three distinct methods are known:

Stoichiometric Carbonyl Reaction. The reaction is very rapid at atmospheric pressure and at mild temperatures. The hydrogen shown in the accompanying equation does not appear in gaseous form but is consumed by side reactions (31,32).

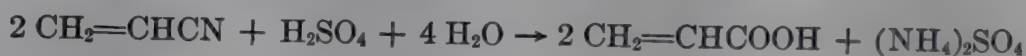


Catalytic Carbonyl Reaction. The catalytic reaction requires elevated temperatures and superatmospheric pressures. Nickel salts or complexes thereof are used as catalysts (31,32).



Semicatalytic Carbonyl Reaction. A catalytic reaction (catalytic as regards nickel carbonyl) of acetylene, carbon monoxide, and water is superimposed upon the stoichiometric reaction of nickel carbonyl, acetylene, water, and acid. In this way the very mild conditions characteristic of the stoichiometric reaction can be used, with a large proportion of the total CO being supplied as carbon monoxide gas, the remainder being supplied in the form of nickel carbonyl (33,34).

Acrylonitrile Method. Care must be exercised in this acid hydrolysis since both the starting acrylonitrile (qv) and the product acrylic acid are polymerizable. The acrylonitrile should remain in the reaction zone and, hence, must be well inhibited. A major advantage of this method is the increase in molecular weight on hydrolysis from 53 to 72, which provides a definite yield improvement (35).

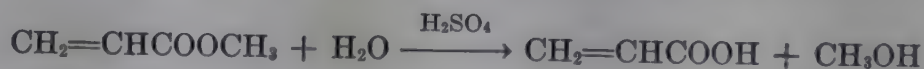


Propylene Method. This recently developed process involves the oxidation of propylene to hydroxypropionic acid; oxides of nitrogen or nitric acid act as catalysts for the reaction (36). Subsequent dehydration yields acrylic acid. The stepwise representation of this process may be shown as follows:



An alternative route is the catalytic oxidation to acrolein, $\text{CH}_2=\text{CHCHO}$, and then to acrylic acid with oxygen and certain metallic catalysts such as Mo, Co, or Ce (37).

Acrylic Ester Method. This method is hampered by the ready polymerizability of the starting material, and the low boiling points of the most available esters and the formed alcohols as compared with that of the product, acrylic acid.



It is generally preferable to saponify the ester to form the corresponding salt.



The salt can then be converted to the acid by either (1) neutralizing the calcium salt with sulfuric acid, removing precipitated calcium sulfate by a difficult filtration procedure, and obtaining the formed acrylic acid in aqueous concentrate; or (2) treating an aqueous solution of the sodium salt with ion-exchange resin to remove sodium ions, removing the resin by filtration, and obtaining an aqueous concentrate of acrylic acid.

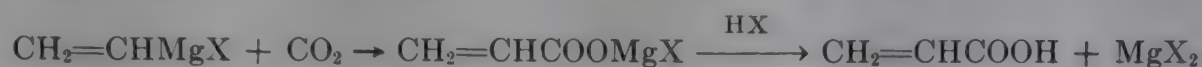
Maleic Acid Method. This patented method involves the decarboxylation of maleic acid to form the desired acrylic acid (38).



Potassium Vinyl Method. The low-temperature conversion of vinyl chloride with potassium metal and a subsequent treatment of the cold vinylpotassium with dry ice is reported to give potassium acrylate in 70% conversion. Customary methods produce acrylic acid (39).



Vinyl Grignard Method. This interesting synthesis involves the use of the well-known carboxylation of a Grignard reagent to form the acid.



ACRYLIC ANHYDRIDE

A very pure grade of acrylic anhydride is obtained by the reaction of sodium acrylate with acryloyl chloride and removal of the formed NaCl.



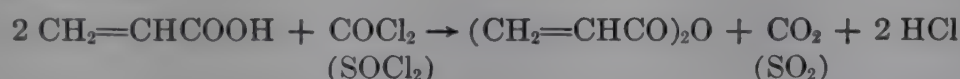
Another method, which involves some chance of cross-anhydride formation, uses the reaction between acrylic acid and acetic anhydride to form the desired product.



The carbonyl reactions (33), mentioned previously under preparative methods for acrylic acid, may be used for preparation of acrylic anhydride by reaction of acetylene and carbon monoxide (as such or in the form of nickel carbonyl) with acrylic acid.



A convenient laboratory method involves the reaction of phosgene (or thionyl chloride) with anhydrous acrylic acid in the presence of a tertiary amine as hydrogen chloride acceptor (40).



ACRYLOYL CHLORIDE

The preparation of acryloyl chloride, a strong lacrimator, from acrylic acid and phosphorus oxychloride results in the formation of phosphoric acid. The phosphoric acid forms a separate layer in which excess oxychloride dissolves and makes purification easier. The preparation from thionyl chloride results in only gaseous by-products, which are readily removed from the reaction zone. Acryloyl chloride can also be prepared by heating 3-chloropropionyl chloride. In all methods, great care should be observed in handling the product to avoid contact and inhalation.



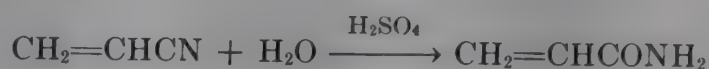
SALTS OF ACRYLIC ACID

Salts have been prepared by (a) the neutralization of acrylic acid with the appropriate base, (b) saponification of the acrylic acid esters (the esters derived from lower alcohols are preferred because of their volatility and greater ease of purification), and (c) the alkaline hydrolysis of acrylonitrile or acrylamide. By one or more

of these methods, salts have been prepared in which the cation is lithium, sodium, potassium, calcium, magnesium, iron, aluminum, zinc, zirconium, lead, and ammonium. These same reactions are applicable to polymeric derivatives.

ACRYLAMIDE

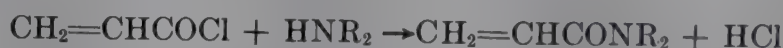
Acrylamide is formed by the partial hydrolysis of acrylonitrile (41). Again care must be exercised to prevent polymerization since both starting and final materials are readily polymerizable.



The carbonyl reactions, discussed under preparative methods for acrylic acid, may be used for preparation of acrylamide from acetylene, carbon monoxide (as such or in the form of nickel carbonyl), and ammonia (42).



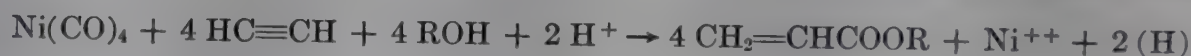
Substituted acrylamides may be prepared from acryloyl chloride and the appropriate amine (43). In this way, such monomers as *N*-acryloylmorpholine, $\text{CH}_2=\text{CH}-\text{COONCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2$, may be formed readily.



ESTERS OF ACRYLIC ACID

Carbonyl Reaction. Under conditions similar to those described under preparative reactions for acrylic acid, a wide variety of acrylic esters may be obtained by using primary, secondary, and even tertiary alcohols as reactants instead of water.

Stoichiometric Carbonyl Reaction. The stoichiometric carbonyl reaction (31) is noteworthy for its rapid rate under very mild conditions, that is, at temperatures usually below 50°C, and with acetylene under atmospheric pressure. The hydrogen shown in the equation below does not appear as such but is consumed in side reactions.



Catalytic Carbonyl Reaction. Elevated temperatures and increased pressures are required in the catalytic reaction (31). Nickel halides or complexes formed from them are used as catalysts.



Semicatalytic Carbonyl Reaction. The reaction of acetylene, carbon monoxide, and an alcohol can be carried out catalytically by supplying these materials to a reacting mixture of nickel carbonyl, acetylene, alcohol, and acid (44). In this manner a major proportion of the total CO used may be carbon monoxide gas, the remainder being in the form of nickel carbonyl. The mild conditions of the stoichiometric carbonyl reaction are adequate for this semicatalytic reaction.

Nickel Carbonyl Preparation (34). The nickel chloride solution is obtained as a recycle stream from the synthesis of the acrylate plus a small amount of new solution to make up for the mechanical and chemical losses in the process (see Fig. 3). The catalyst used is dissolved in the sodium hydroxide solution. The solutions of nickel chloride and sodium hydroxide are pumped through high-pressure injection pumps, and the carbon monoxide is compressed in a four-stage compressor. Nickel carbonyl is

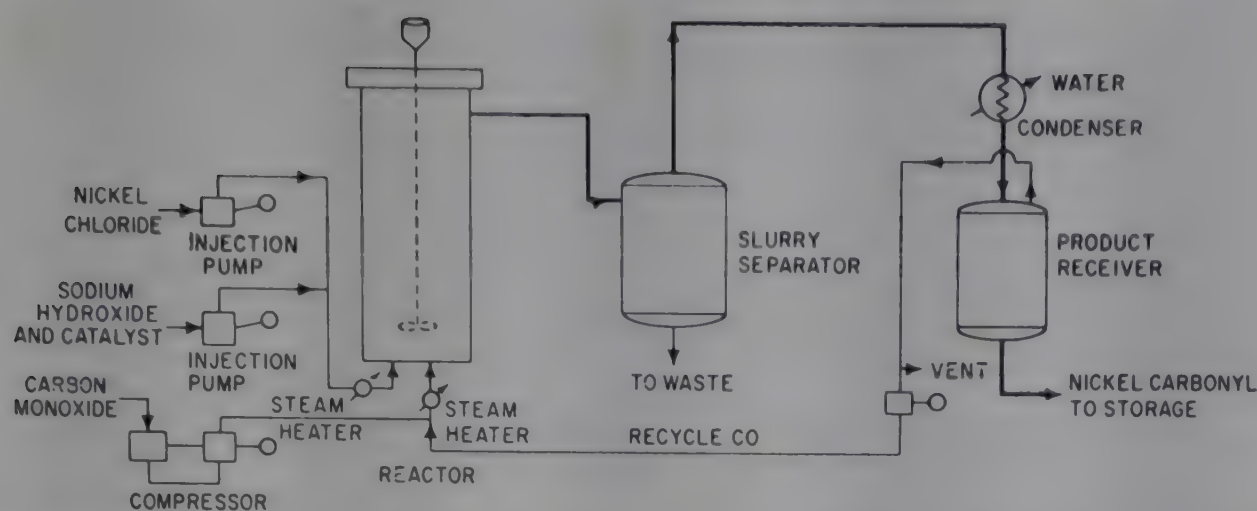


Fig. 3. Flowsheet for the production of nickel carbonyl. Courtesy *Industrial and Engineering Chemistry*.

produced by mixing the solutions with the carbon monoxide at a high pressure in a reactor provided with good agitation. The temperature is maintained above 100°C and the nickel carbonyl leaves the reactor with an excess of carbon monoxide. The carbonyl is condensed and stored under refrigeration and under an atmosphere of carbon monoxide. Excess carbon monoxide is recycled through the process. Inert gases, such as argon, nitrogen, and methane, which accumulate in the gas stream, must be vented to maintain the partial pressure of carbon monoxide above 1500 psi. The liquid slurry from the reaction is discarded after being treated to remove all of the nickel carbonyl. The waste gas streams are passed through a decontamination furnace where they are heated to destroy the nickel carbonyl. This venting of the inert gases provides the major loss of nickel carbonyl, but in spite of this, the yield of carbonyl based on nickel is high.

Methyl or Ethyl Acrylate Preparation (34). The raw materials used for this process consists of nickel carbonyl, carbon monoxide, acetylene, methyl or ethyl alcohol, and hydrogen chloride. These five starting materials are brought together in carefully controlled ratios in a continuous process (see Fig. 4). The reaction to produce the acrylates is carried out in an agitated stainless steel reaction kettle provided with cooling. The reactants are introduced into the vessel under the surface. Preferred conditions include a temperature of 30–50°C; HCl–Ni(CO)₄ equivalent ratio of 1:1.01 to 1:1.2; acetylene–total CO ratio of 1.01:1 to 1.1:1; and an alcohol–total CO ratio of 1.1:1 to 3:1 (alcohol also acts as a solvent to improve fluidity). With five raw materials to be introduced at essentially the same time in correct ratios, instruments for accurately controlling starting material feed rates are important.

Inert gases, impurities in the feeds, and traces of alcohol, nickel carbonyl, and acrylate are scrubbed with alcohol before venting in order to recover usable materials and to remove all traces of carbonyl. The liquid stream from the reactor is stored under refrigeration to prevent polymerization and is then fed continuously to a packed extraction column. Recycled chloride brine enters the top column, extracts the alcohol, salts out the acrylate, and is withdrawn from the bottom of the column. The crude acrylate comes off the top. Material from the bottom of the column goes into a series of distillation columns to separate alcohol and brine and to concentrate the alcohol. The alcohol comes off the top of the final column and is recycled to the process. The brine coming from the bottom of this final column is recycled to the wash

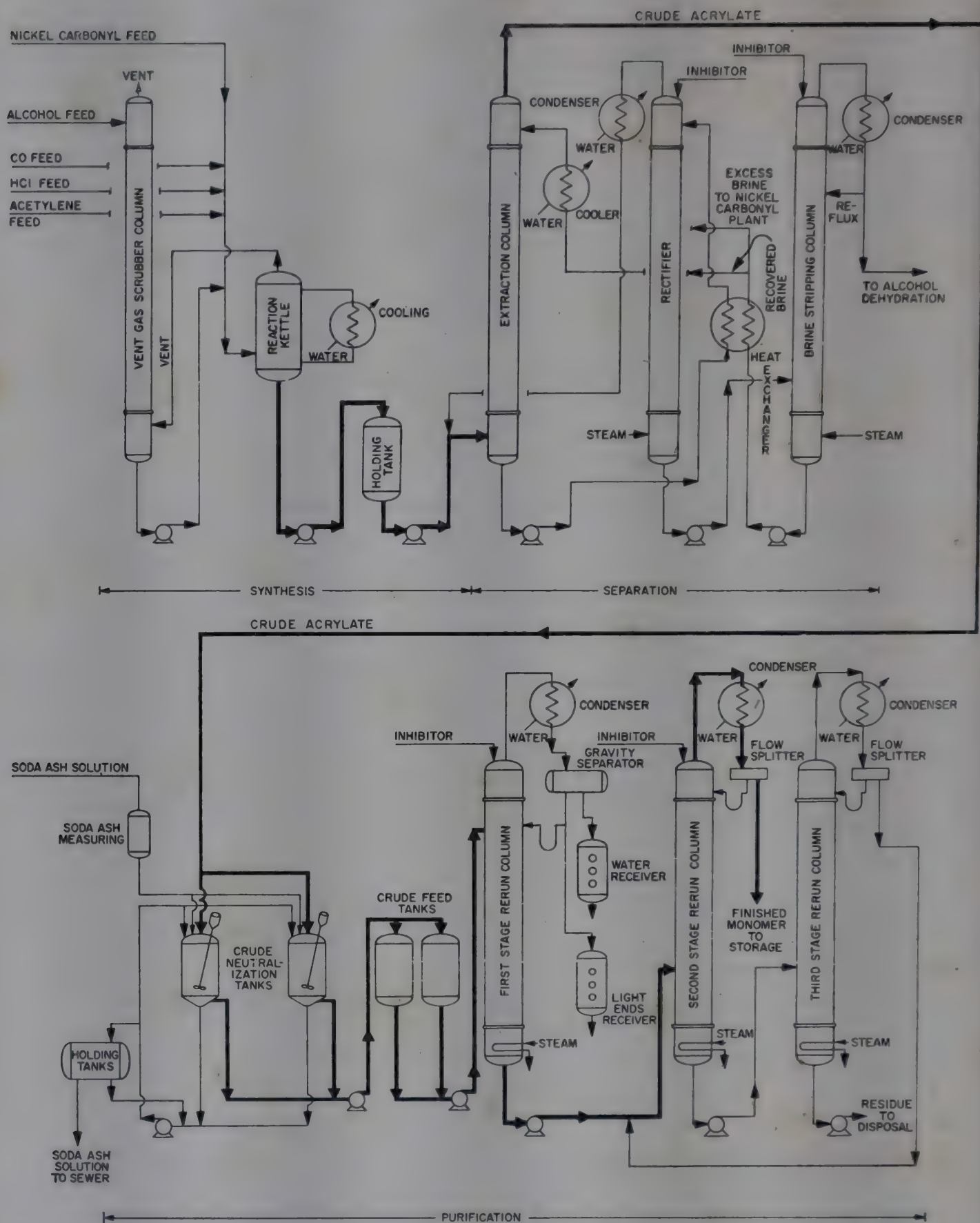


Fig. 4. Flowsheet for the manufacture of acrylate monomers. Courtesy *Industrial and Engineering Chemistry*.

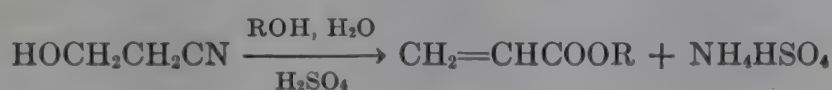
column, and the excess is returned to the nickel carbonyl unit. Process inhibitors are added at the top of the columns to prevent polymerization.

The main stream containing the acrylate is washed batchwise with a soda ash solution to neutralize small amounts of hydrochloric and acrylic acid. The neutralized acrylate solution is fed continuously to a series of columns to produce the final product. In the first column small amounts of water and light hydrocarbons are removed over-

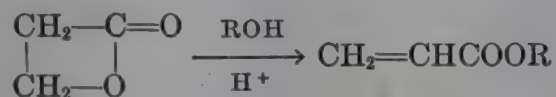
head. In the second column the finished product is removed overhead and the heavy ends, together with some acrylate, leave at the bottom. Process inhibitors are again added to prevent polymerization. Columns are operated under vacuum and acrylate monomer is condensed by means of refrigerated water. The finished monomer, after being mixed with its shipping inhibitor, is stored in large tanks.

Bottoms from the second-stage column are pumped to a third-stage column which is also operated under vacuum. The overhead from this column contains mainly acrylate and is recycled to the first-stage column while the residue, containing polymers and tars, is sent to the decontamination furnace and burned.

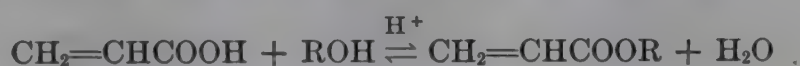
Ethylene Cyanohydrin Process. The process is applied almost entirely to the methyl and ethyl esters (29). For higher esters, acrylic acid is produced first by reaction of ethylene cyanohydrin with water in acid medium, and the acrylic acid is then converted to the higher ester by direct esterification.



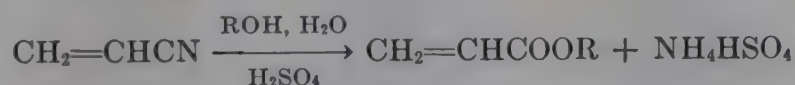
β -Propiolactone Process. β -Propiolactone is obtained by reaction of ketene and formaldehyde. It may be converted directly to acrylic esters by reaction with alcohols or may be converted to acrylic acid (45).



Direct Esterification. In batch procedure, sulfuric acid is normally used as the catalyst and benzene is used as a water entrainer to assist in driving the reaction to completion. The process may also be carried out on a continuous basis (46,47). A vapor phase esterification over silica gel has been disclosed (48).

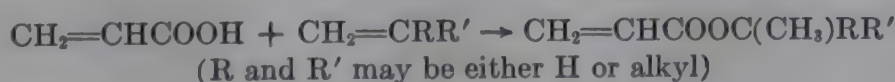


Acrylonitrile Process. Like the ethylene cyanohydrin process, this method is applicable to the preparation of the methyl and ethyl esters. It has not been widely used although numerous patents have been issued.

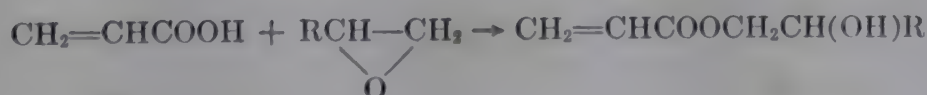


Ester Interchange. This method is useful for the preparation of higher alkyl acrylates from methyl (or ethyl) acrylate (2). Sulfuric acid is commonly used as the catalyst. The reaction is brought to completion by distilling methanol out of the system, in the form of its azeotrope with methyl acrylate.

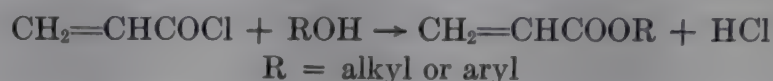
Addition of Acrylic Acid to Olefins. Secondary and tertiary alkyl esters may be made by this method (49,50).



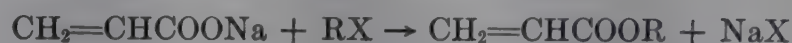
Reaction of Alkylene Oxides with Acrylic Acid (51).



Reaction of Acryloyl Chloride with Alcohols and Phenols. With alcohols, a weak base, such as sodium carbonate or a tertiary amine, is used during the reaction to neutralize the liberated hydrogen chloride and thus prevent its addition to the acrylic double bond. With phenols, a strong base, such as aqueous sodium hydroxide, may be used. Although uneconomical as a manufacturing process, this versatile method is very useful for laboratory preparations (52).

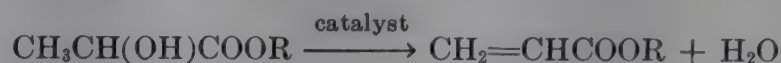


Reaction of Sodium Acrylate with Alkyl Halides. The reaction is particularly useful with active halides, such as benzyl halides (53).

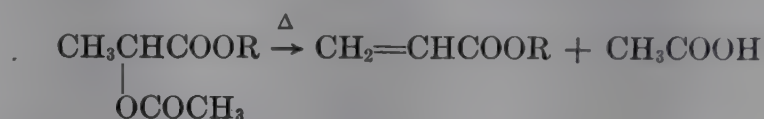


From Lactic Acid Esters.

(a) *Dehydration of alkyl lactates* (54).



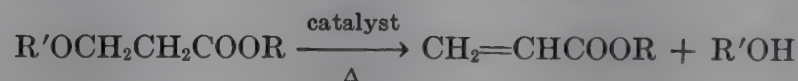
(b) *Pyrolysis of the acetates of alkyl lactates* (55).



Dehydrohalogenation of Alkyl 3-Halopropionates (56). The reaction may be carried out by using catalysts at high temperatures or by treatment with bases.



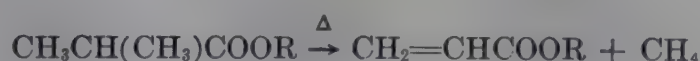
Removal of Alcohol from Alkyl 3-Alkoxypropionates (57).



Condensation of Formaldehyde with Acetates (58). The reaction is carried out at elevated temperatures in the presence of dehydration catalysts.



Pyrolysis of Isobutyrate (59).



Properties of Commercial Monomers

In Table 4 will be found typical properties for the industrially important monomers in the acrylic acid series. The data have been taken from company bulletins. Because of the wide diversity and great number of polymeric products which contain acrylic acid and its derivatives as either the sole or major component, it is not feasible to attempt to itemize the typical properties for such polymeric materials.

Typical properties for acrylamide are as follows:

assay, %	98	iron, ppm	15
water, %	0.8	boiling point, °C,	
water insolubles, %	0.02	at 25 mm Hg	125

Table 4. Properties of Glacial Acrylic Acid and Some Monomers

Property	Glacial acrylic acid	Methyl acrylate	Ethyl acrylate	Butyl acrylate	2-Ethyl-hexyl acrylate
assay, %	99.3	98.8	99.0	99.6	99.5
acidity (as acrylic acid), %		0.0008	0.0008	0.0008	0.02
water (by Karl Fischer), %	0.12	0.06	0.03	0.07	0.10
inhibitors, ^a ppm	200 MEHQ	15, 200, or 1000 MEHQ	15 or 200 MEHQ or 1000 HQ	100 HQ or 50 MEHQ	100 HQ or MEHQ
color (APHA)	5	5	5	5	10
specific gravity, 25/15.6°C	1.045	0.950	0.917	0.894	0.880
refractive index, n _D ²⁰	1.4185	1.4003	1.4034	1.4160	1.4332
distillation range, °C (ASTM D 1078), at 760 mm Hg	140–142				
first drop		79.5	98.8	143.5	213.5
5%		79.8	98.8	145.7	214.8
95%		80.3	100.2	148.0	218.0
last drop		80.8	100.2	149.0	220.0
flash point, °F					
Tag closed cup		26.6	48.2		
Tag open cup		50	50	105	106
Cleveland open cup	155			120	
thermodynamic properties					
latent heat of vaporization, kcal/mole		7.9 ± 0.4	8.3 ± 0.4	9.1 ± 0.5	10.3 ± 0.5
specific heat, kcal/(g)(°C)		0.48	0.47	0.46	0.46

^a HQ, hydroquinone; MEHQ, methyl ether of hydroquinone.

Analytical and Test Methods

In addition to the methods described below, monomer purity is determined by the measurement of other applicable properties, such as refractive index, specific gravity, bromine absorption number as a measure of unsaturation, saponification number for esters, acid number, boiling range, and elementary analysis for those monomers which contain chlorine, nitrogen, or sulfur. Specifications for polymers and copolymers are so diversified as a result of the physical form, molecular composition, molecular weight, and end use of the polymer that no attempt can be made to define the many specification tests employed in their characterization.

Gas Liquid Chromatography (GLC). The operating conditions are given below for the gas chromatographic analysis of ethyl acrylate using a Perkin-Elmer vapor fractometer, model 154-C (60).

temperature, °C	85 ± 1
carrier gas	helium
gas flow, ml/min	50–70 (inlet pressure of 10–20 psi)
column, ft of 1/4-in. tubing	12 (stainless steel or aluminum)
column packing, % iminodipropionitrile	20 (on 30–60 mesh Chromosorb)
detector voltage, v	8.0
sample size, microliters	10
order of elution	(1) ethyl alcohol; (2) ethyl propionate; and (3) ethyl acrylate

A recorded chromatogram of a test sample is compared with the chromatogram of a synthetic sample of approximately the same composition as that of the test sample. Peak heights for impurities are linear in the 0–2% range; hence, quantitative determinations are made using the ratios of peak heights of the unknown sample to the known sample. Peak areas may be used to calculate quantitative data if desired.

Pyridine Sulfate Dibromide (PSDB) Method. This method, adapted from the procedure reported by Rowe, et al. (61) for determining unsaturation in tall oil, is applicable to the determination of the purity of monomeric acrylic and methacrylic acids and esters. The purity is measured by bromine addition at the double bond. A solution of pyridine sulfate dibromide ($\text{C}_5\text{H}_5\text{N} \cdot \text{H}_2\text{SO}_4 \cdot \text{Br}_2$) in glacial acetic acid is used as the bromine-addition reagent, with mercuric acetate as catalyst. The excess reagent is measured by adding potassium iodide and titrating the liberated iodine with sodium thiosulfate.

Saponification Number. The saponification number is defined as the number of milligrams of potassium hydroxide required for the saponification and neutralization of one gram of sample. The saponification number is determined by allowing the sample to react with a measured excess of $N/2$ alcoholic potassium hydroxide and then determining the amount of potassium hydroxide which has reacted with the sample by titrating the excess alkali with standard aqueous acid.

Purity. The purity of glacial acrylic acid is determined by direct titration with $N/2$ sodium hydroxide.

Health and Safety Factors

Acute and chronic local and systemic toxicity data are listed in Table 5. It should be noted that all have fairly high ratings and should be handled with adequate ventilation and with techniques designed to eliminate inhalation, ingestion, and contact with skin and clothing. With reasonable care, no toxicity problems should arise, as evidenced by the many years of production and use experience in large-scale industrial applications. Because of the relatively low flash point of some of the monomers, care should also be exercised in regard to flammability. The strong tendency of all of these monomers to polymerize should be borne in mind in all handling operations.

The toxicity data presented in Table 5 are based on a 0–3 rating system in which 0 = no toxicity, 3 = severe toxicity, and U = unknown (62).

Table 5. Toxicity Data for Acrylic Acid and Some Monomers

Toxicity	Acrylic acid	Acrylamide ^a	Ethyl acrylate ^b	Butyl acrylate
acute local				
irritant	3	3	3	2
ingestion	3	3		2
inhalation	3	3		
acute systemic	U	U	3	2
chronic local	U	U	U	U
chronic systemic	U	U	U	U

^a Acrylamide can be absorbed through the intact skin. Animal experiments suggest that the toxic effect may be upon the central nervous system.

^b Topical application to the intact skin of rabbits caused marked local irritation; exposure to vapors produced irritation of the mucous membranes of the eyes, nose, and mouth. An oral dose of 0.42 g/kg of body weight was fatal to rabbits.

No toxicity data are available for methyl acrylate, but it is thought that this monomer will follow much the same pattern as that outlined for ethyl acrylate (63,64). 2-Ethylhexyl acrylate is slightly toxic.

Storage of uninhibited monomers should be carried out under refrigeration, and excessive heat should be avoided even with inhibited monomers. Material containing peroxides should not be stored. Uncontrolled polymerization of undiluted monomers can be violent and explosive. The thawing of frozen inhibited monomers should, obviously, be carried out with care. Under adequate care, no problems should be encountered, but a review of the heat of polymerization data in a later section will give ample evidence of the potential danger that carelessness can produce.

Polymers of Acrylic Acid and Its Derivatives

As is the case with other addition polymers, the polymerization of acrylic acid and its derivatives is an exothermic reaction. Whatever the initiating species, the heat liberated by the polymerization of each monomer is a definite and measurable value, called the *heat of polymerization*. Such values are listed in Table 6 and show the amount of heat that must be accounted for in each polymerization. This heat may be allowed to dissipate slowly by controlling the rate of polymerization, or the polymeriza-

Table 6. Free Radical Polymerization Data^a

M ₁ ^b	r ₁	r ₂	Q	e	Heat of homo- polymerization of M ₁
acrylic acid	0.19	0.22	0.22	1.09	18.5
methyl acrylate	0.14	0.68	0.43	0.73	18.7
ethyl acrylate	0.16	1.01	0.34	0.58	18.7
butyl acrylate	0.21	0.82	0.43	0.53	18.5
2-ethylhexyl acrylate	0.26	0.94	0.41	0.39	
acrylamide			1.18	1.30	13.8, ^c 19.8
sodium acrylate			0.71	-0.12	
methyl α-chloroacrylate			2.02	0.77	

^a All data established at 60°C.
^b M₂ is styrene, for which Q is 1.0 and e is -0.8.
^c Reference 67.

tion may be carried out in a medium that will remove the heat of polymerization without permitting a violent or dangerous reaction. All polymerization types will be discussed subsequently. Also listed in the table are the Price-Alfrey Q and e values, parameters for each monomer, from which can be determined, by standard techniques, the way in which such monomers will behave in the preparation of copolymers. For the comonomer system, M₁ and M₂, derived values for the monomer reactivity ratios, r₁ and r₂, will show the statistical chance for M₂ or M₁ to add to the growing polymer chain ending in either an M₁ radical or an M₂ radical. In this way it can be determined whether or not copolymerization is possible, and, if it is, whether there is random distribution of the monomer units in the polymer chain, or a tendency to alternate or to form blocks of individual monomer types. Control of addition rates of individual monomers makes it possible to achieve a desired polymer composition (65,66).

Illustrative data are given in Table 6 for copolymers of styrene with various acrylic monomers (13).

In order to avoid the premature polymerization of these monomers during storage and shipment, inhibitors or refrigeration are employed. A wide variety of inhibitors is available (14). Among those in common use for acrylic acid and its esters are hydroquinone and the methyl ether of hydroquinone. It is customary to inhibit the monomers to assure safe storage and handling, but it is possible to use minimal concentrations that allow subsequent polymerizations to be conducted without removing the inhibitor, thus avoiding an extra manipulative procedure.

Both the molecular weight and the molecular weight distribution of the polymer are very important considerations. Absolute values for the number average and weight average molecular weights are obtained by osmometry and light scattering techniques; the greater the ratio of these two values, the wider the molecular weight distribution. Viscometric determinations can be used to obtain polymer molecular weights by the determination of the k and α values in the Mark-Houwink equation relating intrinsic viscosity $[\eta]$ to molecular weight.

$$[\eta] = kM^\alpha$$

Values for k and α are listed in Table 7 with the solvent used in each case. Intrinsic viscosities are normally determined by plotting polymer concentration, in g/100 ml, against either or both (a) (relative viscosity - 1.0)/(polymer concentration, in g/100 ml) and (b) (natural logarithm of the relative viscosity)/(polymer concentration, in g/100 ml). Extrapolation of this plot to zero concentration gives the intrinsic viscosity in deciliters per gram. It is more difficult to obtain satisfactory data for the ionic polymer, poly(acrylic acid), but in appropriate solvents, adequate constants

Table 7. Viscometric Molecular Weight Constants

Polymer from	k	α	Solvent, at 30°C	Bibliography reference
acrylic acid	85×10^{-5}	0.50	dioxane	(68)
acrylamide	37.3×10^{-5}	0.66	1N NaNO ₃	(72)
methyl acrylate	4.5×10^{-5}	0.78	benzene	(13)
methyl acrylate	5.5×10^{-5}	0.77	acetone (25°C)	(69)
ethyl acrylate	27.7×10^{-5}	0.67	benzene	(70)
ethyl acrylate	20×10^{-5}	0.66	acetone	(71)
ethyl acrylate	31.4×10^{-5}	0.68	chloroform	(70)

have been reported. In a significant contribution, Katchalsky has shown that a homopolymer of methyl acrylate can be hydrolyzed to the polyacid in aqueous acetic acid with *p*-toluenesulfonic acid and the poly(acrylic acid) converted to the methyl ester by treatment with diazomethane (16). Molecular weight determinations are mutually corroborative and show that no polymer degradation has taken place in the process. Thus, for such ionic species, two routes are open to the determination of molecular weights (a) use of k and α constants in appropriate solvent media, and (b) conversion to the methyl ester with diazomethane and use of somewhat more conventional viscometric values in organic solvent media.

PREPARATION OF POLYMERS

Monomers of the acrylic acid series are generally polymerized with ease. Because of this ready polymerizability, safe storage and handling of the monomers require refrigeration of the monomers or the addition of minor proportions (0.2% or less) of polymerization inhibitors. The polymerization process may require the separation of the inhibitor from the monomer in question by distillation, or by washing; in many cases, the process can be effected in the presence of the inhibitor. Polymerizations may be carried out in bulk, in aqueous or organic solvent solution, in emulsion, or in aqueous dispersion (73-75). Derivatives of these polymers can also be prepared by chemical alteration of the polymer functionality. In each case, the polymerization is effected by means of a suitable initiator system. The particular type of initiator system is governed by the polymerization method, and may include free radical initiation (produced by either thermal or oxidation-reduction operations, or by radiation techniques), anionic initiation (76), and organometallic initiation. Molecular weight may be controlled by the customary methods of choice of solvent or polymerization medium, concentration of monomer in solution, concentration of initiator, temperature of polymerization, the use of chain-transfer agents, such as mercaptans, alcohols, and chlorinated compounds, as well as by certain methods peculiar to individual polymerization processes, which are mentioned in subsequent sections.

Acrylic Acid Polymers. The solution polymerization of acrylic acid may be carried out in water by heating the aqueous monomer in the presence of an initiator, such as hydrogen peroxide, potassium persulfate, or acetyl peroxide, or by initiating a redox polymerization at reduced temperatures with a system composed of potassium persulfate and sodium thiosulfate as the oxidizing-reducing pair. Molecular weight may be controlled by the use of a special chain regulating system consisting of sodium hypophosphite, $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$, and copper acetate (77), as well as by the conventional means. Polymer solutions in organic solvents, such as methanol and dioxane, may be prepared by the use of azobisisobutyronitrile initiator at elevated temperatures. A solution of acrylic acid in such solvents as benzene and *n*-hexane may be polymerized with an initiator, such as benzoyl peroxide, at elevated temperatures to produce an insoluble polymer which may be removed from the reaction medium by filtration.

The bulk polymerization of acrylic acid can be carried out by carefully warming the monomer containing benzoyl peroxide, but great care must be taken to prevent a runaway polymerization since there is no solvent medium to take up the heat of polymerization. Polymerization of the acid in the frozen state has been conducted by irradiation of the solid material with a ^{60}Co source (78).

Poly(acrylic acid) has also been prepared by reactions on other preformed polymers. Polymeric acrylic esters may be hydrolyzed to the acid by heating an aqueous acetic acid solution of the polymer, under a nitrogen blanket, in the presence of *p*-toluenesulfonic acid. Similarly, polyacrylonitrile has been hydrolyzed by warming a concentrated sulfuric acid solution of the polymer, with subsequent isolation by precipitation from aqueous dilute sulfuric acid. Alkaline hydrolysis of a poly(alkyl acrylate) and of polyacrylonitrile produces the corresponding salt of poly(acrylic acid), which can be recovered in aqueous solution by treatment with an ion-exchange resin to remove ions, such as sodium and potassium.

Polymers of Acrylic Acid Salts. Aqueous solution polymerizations of such salts as sodium and calcium acrylate may be carried out by thermal or redox free-radical

techniques, although data (79) have been published showing different polymerization rates for the ionized and unionized forms of acrylic acid. Specialized techniques have been developed for these polymerizations. Two of these techniques combine the simultaneous polymerization and either the spray or drum drying of the aqueous monomeric salt in the presence of an initiator, such as ammonium persulfate, to produce a solid polymer (80). Polymerization of the monomer preslurried with preformed polymer serves to control the exothermic reaction. Solid state polymerizations have been carried out by ^{60}Co source irradiation of the solid monomeric salts and polymerization by a free radical mechanism. By freezing the irradiated monomer it has been possible to store the trapped free radicals and subsequently to initiate polymerization by allowing the monomer to warm to ambient temperature. The energy released by a chemical reaction has been used to initiate polymerization in the case of an aqueous ethanol-moistened mixture of solid sodium acrylate and a salt, such as lithium chloride (81). Characteristics reported for this type of polymerization include the need for complete exclusion of air, the inability to inhibit polymerization by the customary inhibitors, and decreased molecular weight with lowered temperatures.

Mixed salts, eg, poly(sodium acrylate-calcium acrylate), have been prepared. It has been demonstrated that the copolymerization of sodium acrylate with minor proportions of calcium acrylate proceeds at a more rapid rate and to a higher molecular weight than either monomer alone (82).

Salts of poly(acrylic acid) can also be produced by reactions on preformed polymers. For instance, neutralization of homo- and copolymers containing acrylic acid units can be carried out with inorganic and organic bases to produce soluble products. When volatile organic bases are used to solubilize water-insoluble acidic copolymers, the loss of the base by evaporation can leave films and coatings of limited water sensitivity. Alkaline hydrolysis of poly(alkyl acrylate), polyacrylonitrile, and polyacrylamide results in the formation of the corresponding polymeric salt. Partial hydrolysis can also be used to prepare corresponding copolymers. Cosaponification with mixed bases has been used to prepare the mixed salts mentioned above (83).

Acrylamide Polymers. The solution polymerization of this monomer may be carried out in aqueous medium (84) by the use of an initiator, such as potassium persulfate, at 60–100°C, or by a reaction with potassium persulfate-sodium thiosulfate redox system initiated at room temperature. In either case, molecular weight control can be achieved by altering the concentration of the initiator and by the inclusion of chain regulators. Solution polymerizations are also carried out in methanol with azobisisobutyronitrile as the initiator at a temperature of 50–100°C. Molecular weight is controlled by the addition of various amounts of 2-propanol to the methanol solvent; the more 2-propanol, the lower the molecular weight. Polymerization in the solid state has been reported for ^{60}Co irradiated acrylamide.

Copolymers of acrylamide with acrylic acid are prepared by the methods outlined above. Copolymerization with acrylic salts has been reported for the spray and drum polymerization techniques described previously. It has been demonstrated in this work that increments of acrylamide increase the rate of polymerization of the acrylic salts. Such copolymers can also be prepared by partial alkaline hydrolysis of the acrylamide homopolymer (85).

Acrylic Ester Polymers. Esters of acrylic acid can be polymerized in solution by heating the particular monomeric ester in a solvent, such as benzene, acetone, ethyl acetate, or 2-propanol, in the presence of an initiator, such as benzoyl peroxide,

azobisisobutyronitrile, or *t*-butyl hydroperoxide. As the alkyl group of the acrylic ester increases in size, solubility differences will be observed. Copolymerization with other acrylic esters, acrylic acid, methacrylic acid, and other comonomers may also be conducted in the same general manner. Molecular weight control is effected by choice of solvent and polymerization temperature, amount and kind of initiator, and the use of a chain regulating agent, for example, *t*-dodecyl mercaptan, or chloroform.

The emulsion polymerization of acrylic esters, alone or with other comonomers, offers a convenient method for the preparation of high-solids, low-viscosity latexes. The emulsion polymerization system may be represented as follows. A monomer emulsion is prepared from 30 parts of ethyl acrylate, 70 parts of water, and 3 parts of sodium lauryl sulfate. With the emulsion agitated and the batch temperature adjusted to 20°C, in rapid succession are added 0.3 parts of potassium persulfate and 0.3 parts of sodium metabisulfite. Within a space of one-half hour, the batch temperature will rise to about 80–85°C. The polymerization is complete at this point. The permissible concentration of the monomer is obviously a function of the heat of polymerization; if enough heat is produced to boil the water and unreacted monomer, a dangerous situation results. Alternatively, the polymerization can be effected by adding the monomer to the water and emulsifier at an elevated temperature in the presence of an initiator, for example, ammonium persulfate, with the monomer added at such a rate as to prevent a runaway polymerization. The choice of an emulsifier is very important and will depend upon the monomer or monomers employed and the emulsion stability required. Anionic, cationic, and nonionic emulsifiers are satisfactorily employed under certain conditions, and a recent concept involves the determination of the hydrophil-lipophil balance (HLB) as a yardstick for the choice of emulsifying agent (86). Molecular weight is controlled by the choice of emulsifier and initiator and by the use of such chain regulator types as mercaptans, certain halogenated compounds, and alcohols.

Acrylic ester polymers are prepared in suspension by the use of a protective colloid or an inert suspending medium in an aqueous system and thermal polymerization of the monomer with a lipophilic initiator, for example, benzoyl peroxide or lauroyl peroxide. The polymer so produced may be removed from the suspension by filtration and thus isolated as a solid. Some suspensions can be stabilized by the addition of an appropriate colloid.

Crystalline acrylic polymers also have been prepared (87). Syndiotactic poly(isopropyl acrylate) was prepared by a very low temperature (–100°C) free radical polymerization. Isotactic polymer was prepared with a Grignard initiator, and then hydrolyzed to a presumably isotactic poly(acrylic acid) with *p*-toluenesulfonic acid in aqueous acetic acid (88). Stereospecific *N*-substituted acrylamide polymers have also been prepared.

Mixed polymer systems can be prepared in three different ways. Copolymers are prepared by the copolymerization of a mixture of the monomers in question. Physical blends of two or more homopolymers can be made under conditions in which the polymers involved are compatible. Finally, graft copolymers are formed by polymerization under appropriate conditions of a monomer or monomers in the presence of a preformed polymer. In this way, polymer systems with the same overall content of monomers A, B, and C can be prepared, but the properties of the three systems may be completely different. Thus, not only the gross monomer composition but the method of preparation play an important and significant role in the performance and use properties of the composition in question.

PROPERTIES OF POLYMERS

Physical Properties. Homo- and some copolymers which contain acrylic acid and salt groups exhibit a definite hydroplasticity. Small amounts of water plasticize films of these polymers so that, instead of the hard and brittle anhydrous film, a tough, nontacky, clear film is obtained. This hydroplasticity can be imparted by varying the relative humidity of the ambient atmosphere.

Polymeric acrylic esters are thermoplastic, and the glass transition temperatures (T_g) given in Table 8 show the variation of this property with the size of the alkyl group, and also show the effect of branching. The values reported are for certain homopolymers. It is important to remember that modified hydrophilicity, softening point, tensile strength, solubility, and hydrolytic stability can be achieved by copolymerization with other acrylic derivatives and other polymerizable comonomers. Physical properties and chemical reactivity can also be modified by the degree and kind of crystallinity of the particular polymer.

Table 8. Glass Transition Temperature

Homopolymer	T_g , °C	Bibliography reference
acrylic acid	106	(90)
methyl acrylate	8	(89)
ethyl acrylate	-22	(90)
	-24	(89)
<i>n</i> -propyl acrylate	-45	(90)
isopropyl acrylate	-8	(89)
<i>n</i> -butyl acrylate	-56	(89,90)
isobutyl acrylate	-40	(90)
<i>tert</i> -butyl acrylate	43	(89,90)
<i>n</i> -octyl acrylate	-80	(90)
2-ethylhexyl acrylate	-70	(90)
	-55	(89)
<i>n</i> -tetradecyl acrylate	20	(90)
<i>n</i> -hexadecyl acrylate	35	(90)
acrylonitrile	96	(89)
	110	(90)

The minimum film forming temperatures (MFT) of copolymers can be changed markedly by alteration in the ratio of the comonomers (91). This is also accompanied by a change in the hardness of formed films, and these changes are shown in Table 9 for emulsion copolymers of ethyl acrylate (EA) and methyl methacrylate (MMA). The hardness was measured with a Tukon instrument and is reported as the hardness number, KHN.

Other physical properties of homopolymers of the acrylic acid esters vary with the particular alkyl acrylate employed. Illustrative data are listed in Table 10 (14).

Mildly crosslinked polymeric acid and poly(acrylic acid)-poly(vinyl alcohol) blends exhibit a property based upon the reversible extensibility of the polymer chain, known as pH muscle action or *tieno* polymer behavior (92,93). A polyacid in the unionized form retains a coiled configuration, but the neutralized polymer exists in an elongated configuration as a result of the mutual repulsion of neighboring electrostatic charges on the ionized polymer backbone. Thus the chain configuration is a

Table 9. Copolymer Film Properties

Weight ratio EA:MMA	T_g , °C	MFT, °C	KHN
100:0	-23		
70:30	0	<10	0.6
55:45		17	3.8
50:50	23		
45:55		32	8.2
35:65		49	13.1
30:70	55		
10:90	82		
0:100	105	90+	22

Table 10. Properties of Several Polymers of Acrylic Acid Esters

Polymer from	Elongation, %	Tensile strength, psi	H ₂ O absorption, %/24 hours
methyl acrylate	750	1005	18.8
ethyl acrylate	1800	33	13.1
butyl acrylate	2000	3	8.4

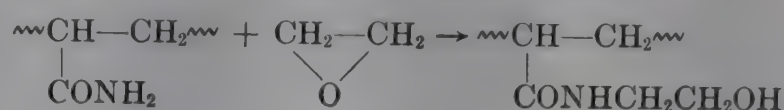
function of the ambient hydrogen ion concentration. It has been shown that chemical changes can thus be converted into mechanical work. Thin fibers of the poly(acrylic acid)-poly(vinyl alcohol) blend, maintained in an aqueous medium, change in length and raise or lower suspended weights upon change in the pH of the ambient medium. Similarly, mechanical work can be converted to chemical energy. Stretching of such a thin fiber results in a change of as much as 0.2 units in the pH of the surrounding aqueous medium. The theoretical and practical implications of this phenomenon are important, and the suggestive correlation with muscular activation in animals is noteworthy.

Chemical Reactions. In general, the reactions of the polymers may be said to be about the same as those of the monomers, except that inter- and intrachain interactions add another parameter, and the completeness of the reaction is affected by chain configuration and molecular weight of the polymer. Obviously, reactions of copolymers are even more complicated than those of homopolymers (94).

The polyacids are readily neutralized with various inorganic and organic bases. With monovalent cations, the solution viscosity is generally increased because of the chain extension induced by electrostatic repulsion. In the case of polyvalent cations, insolubilization of the neutralized polymer can result. Organic bases may be used to impart modified solubility and varied hydrophil-lypophil balance. The polyacids can be esterified directly with alcohols and by reaction with alkylene oxides, although forcing these reactions to completion is difficult. The most complete esterification is obtained by treating the polyacids with diazomethane to form the methyl ester (16). Polyacid interaction with fillers and other polymers has also been reported. Complexes are formed from poly(acrylic acid) and high molecular weight polyoxyethylene glycols (95). Insoluble complexes are formed from poly(acrylic acid) and polyvinylpyrrolidone, although this complex is readily solubilized in water with traces of ammonia. Complexes with montmorillonite clay have also been reported. This is reminiscent of the soil conditioning effort, which involved improvement in the tilth of

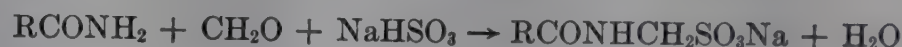
agricultural soils by the incorporation of various polyelectrolytes and consequent amelioration of soil water retention and seedling emergence. Insoluble films and products are formed by the interaction of polyanionic materials, poly(acrylic acid), and polycationics, poly[2-(dimethylamino)ethyl acrylate].

In addition to hydrolysis, homo- and copolymers of acrylamide also undergo certain interesting chemical modifications (96). The addition of an alkylene oxide imparts surface-active properties to the derived product, and this transformation may be represented as follows in the case of ethylene oxide (97).



Reaction with formaldehyde results in the formation of the corresponding *N*-methylol derivatives; such reaction products contain active sites for further reaction, including crosslinking and resultant insolubilization.

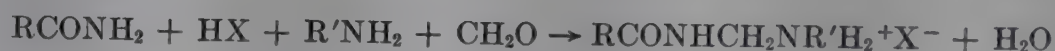
Sulfomethylation may be carried out in either a stepwise sequential manner or a simultaneous operation, and may be varied considerably in scope. However, the overall reaction may be represented by the following scheme where R represents the backbone of a polymer chain containing amide side chains.



The Hofmann degradation can be carried out at room temperature by reaction of the polymeric amide, eg, polyacrylamide, with sodium hydroxide, and sodium hypochlorite, and the reaction may be represented as follows, with R standing for the polymeric backbone of the acrylamide polymer.



The Mannich reaction for polyacrylamide has also been reported. With a secondary amine, hydrohalide (HX), and formaldehyde, the following polymeric amine salt is obtained.



Polycationic products, such as those obtained by homo- or copolymerization of 2-(dimethylamino)ethyl acrylate, can, of course, be neutralized with inorganic, organic, and polymeric acids, such as sulfuric, acetic, and polyacrylic, respectively, in addition to the usual saponification noted for polymeric acrylates. These polymeric tertiary amines can also be quaternized with reagents such as methyl hydrogen sulfate (98) to form the corresponding quaternary ammonium derivatives.

Uses and Economic Aspects

Although the acrylic monomers find some use as chemical intermediates, they are chiefly important for their homo- and copolymers. The physical and chemical properties of the polymers derived from acrylic acid and its derivatives run the gamut; the already wide range of properties present in the polymers of the various available monomers is expanded greatly by the preparation of copolymers of these and nonacrylic modifying monomers. The acrylics, often used in conjunction with the methacrylic derivatives, may comprise major or minor proportions of polymers used in the fields of application shown in Table 11.

Table 11. Uses of Acrylic Acid

plastics	printing inks	masonry sealers
paper manufacture and coating	interior wall paints	lubricating and fuel oil
exterior house paints for wood and	floor polishes	additives
masonry	floor and wall coverings	lacquers for automotive,
coatings for compressed board and	industrial primers	appliance, and furniture
related building materials	textile sizing, treatment, and	finishes
flocculation of mineral ore fines and	finishing	pharmaceutical binders
waste water, and treatment of	leather impregnation and fin-	hot metal coatings
sewage	ishing	

No data have been published by the U.S. Tariff Commission on the production or sales of either the monomers or polymers of acrylic acid and its derivatives. However, estimates have been made to show the growth, in pounds, of total acrylate and methacrylate monomer production since the initial commercial introduction of these materials in the 1930s.

1940	3,000,000
1943	37,000,000
1944	50,000,000
1959	150,000,000

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ACRYLIC AND MODACRYLIC FIBERS

An acrylic fiber, as defined by the Federal Trade Commission (1), is a manufactured one "in which the fiber-forming substance is any long-chain synthetic polymer composed of at least 85% by weight of acrylonitrile units ($-\text{CH}_2-\text{CH}-$)." A



modacrylic fiber is one "composed of less than 85% but at least 35% by weight of acrylonitrile units." Typical acrylic fibers produced in the U.S. are Orlon (Du Pont), Acrilan (Chemstrand), Creslan (American Cyanamid), and Zefran (Dow).

Verel (Tennessee Eastman) and Dynel (Union Carbide) are classified as modacrylics. (These names are registered trademarks.)

Acrylic Fibers

Polyacrylonitrile has been known in the German patent literature since the late 1920s, but its instability at the melting point and the lack of suitable solvents prevented its use in synthetic fibers, by making either melt spinning or solution spinning impossible. In 1938, H. Rein of I. G. Farbenindustrie described fibers obtained from the polymer dissolved in aqueous solutions of quaternary ammonium compounds, such as benzyropyridinium chloride (2), or of metal salts, such as lithium bromide, sodium thiocyanate, and aluminum perchlorate (3). The Du Pont Company studied the suitability of many solvents (4) and started developing Fiber A in the early 1940s.

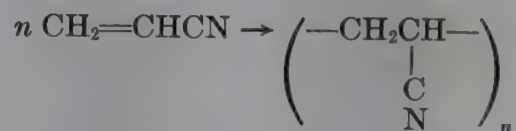
The first commercial acrylic fiber was produced by Du Pont in 1948 under the name of Orlon. Since then, acrylic fiber production has experienced a spectacular growth. The Chemstrand Corporation started producing Acrilan in 1952, and Dow Chemical Company and American Cyanamid joined the field with Zefran (1958) and Creslan (1959). In 1960, 116,000,000 pounds of acrylics were shipped from United States plants alone (5). There are also many foreign producers (see Table 7, p. 328).

PROPERTIES

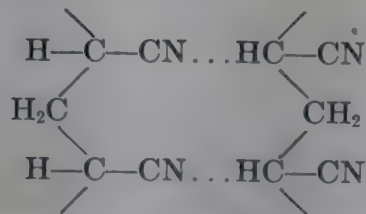
Some of the more important intrinsic fiber properties are discussed here, whereas those properties that are related to fabrics, such as warmth, hand, and launderability, are discussed in the section on Uses (p. 331).

The properties of the fibers themselves are largely dependent on several factors: the structure of polyacrylonitrile, the kind and amount of modifier, the spinning method, and the degree of stretching during fiber formation. The last two items affect the molecular orientation and the crystallinity of the fiber to a large degree.

Polymerization of acrylonitrile proceeds by the successive addition of acrylonitrile monomer units, resulting in large, linear molecules,

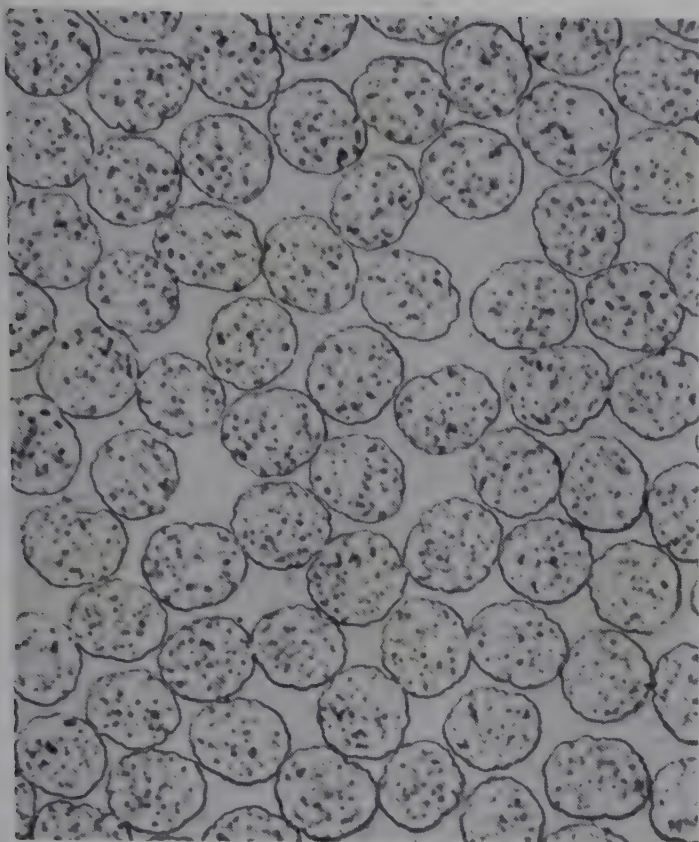


where n may range from 500 to 5000. For commercial fibers, n is normally in the range of 600–2000, equivalent to molecular weights of 32,000–110,000. On the basis of x-ray and solubility studies, it is commonly accepted that adjacent chains are held together by hydrogen bonding according to the following scheme (6):

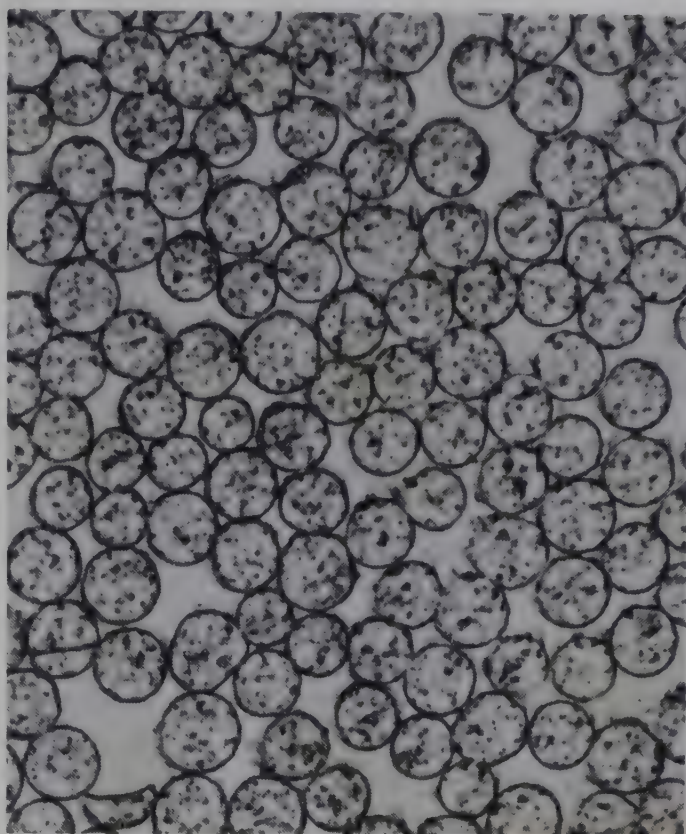


There are some, however, who prefer the concept of a strong and specific interaction between pairs of CN groups; this has been referred to as a CN dipole-pair bond (7).

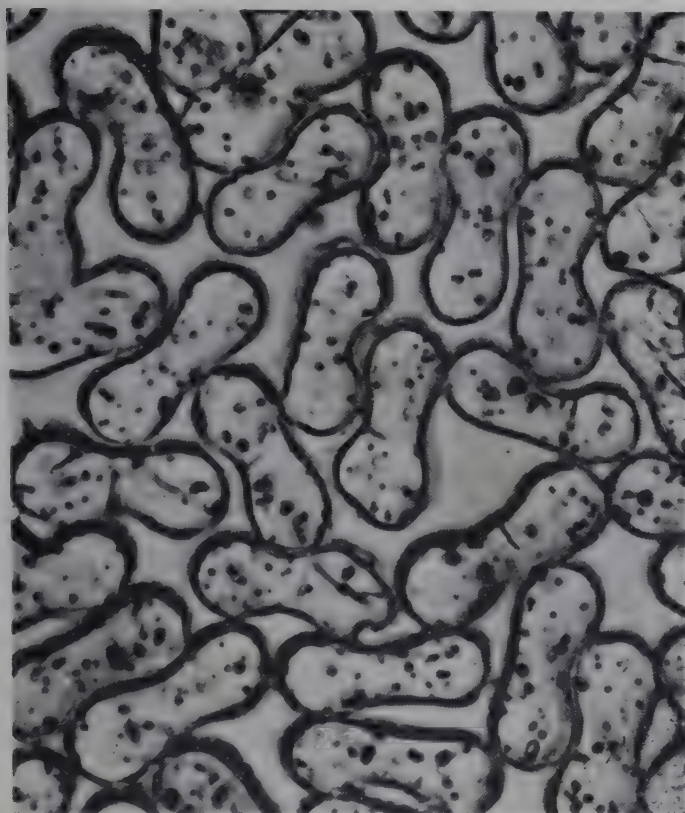
Fibers of 100% polyacrylonitrile are rarely used commercially because of difficulty in dyeing. To overcome this characteristic, acrylonitrile is copolymerized with at least one other monomer. The resulting, more open, structure aids dye penetration



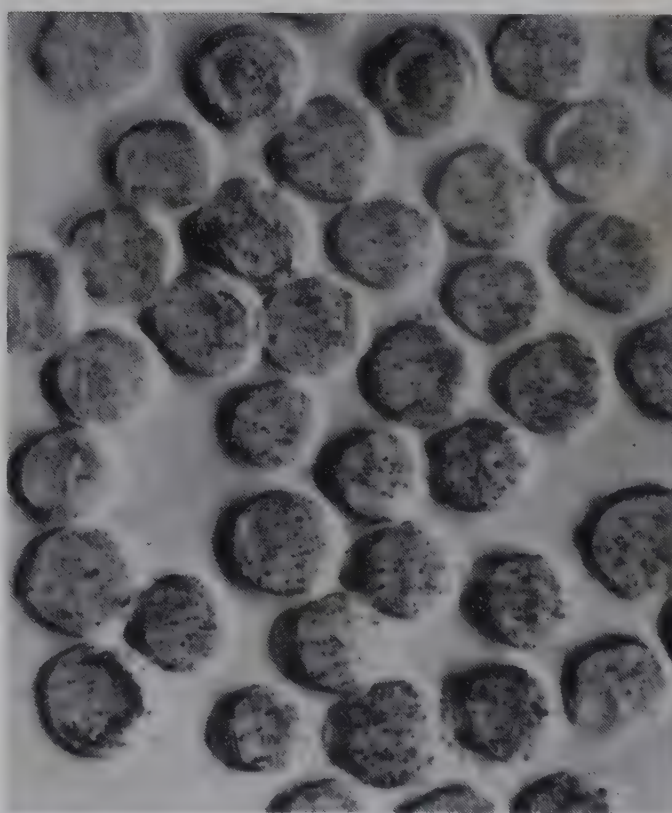
Acrilan
Courtesy The Chemstrand Corporation.



Creslan
Courtesy American Cyanamid Company.



Orlon
Courtesy E. I. du Pont de Nemours & Co., Inc.



Zefran
Courtesy Dow Chemical Company.

Fig. 1. Photomicrographs of cross sections of some acrylic fibers.

of the fiber. Alternatively, other constituents (including other polymers or copolymers) may be incorporated by blending with polyacrylonitrile or copolymers of acrylonitrile before spinning. Dye sites for dyestuffs may be introduced by either of the above procedures.

Acrylic fibers are produced by wet- or dry-spinning methods. Melt spinning is not possible because of polymer degradation at temperatures below or at the melting

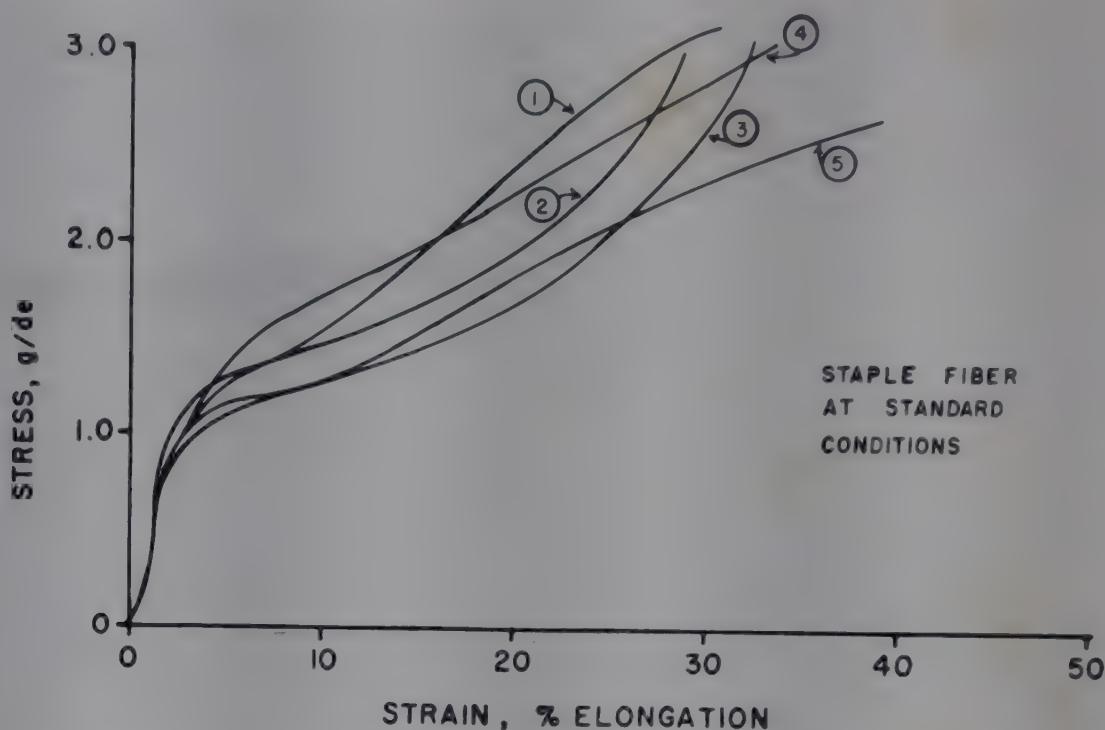


Fig. 2. Stress-strain relationships for some acrylics (8,9). ① Orlon (Du Pont). ② Creslan (American Cyanamid Company). ③ Zefran (Dow Chemical Company). ④ Tacryl (Stockholms Superfosfat Fabriks AB). ⑤ Acrilan (Chemstrand Corporation).

point. In dry spinning, the cross section is usually dogbone in shape. In wet spinning, coagulation results in a round or bean-shaped cross section, although ribbon sections are obtained in some cases.

Physical Properties. Some of the more important physical properties (10a) of the acrylic fibers are presented in Figures 1 and 2 and in Table 1.

Acrylic fibers are manufactured in the form of continuous-filament yarn, staple, and tow. Staple length varies depending on the type of spinning system used to convert the fiber into spun yarn. In the United States, lengths vary from $1\frac{1}{4}$ inches for the cotton system to 6 inches for the worsted system.

Cross sections of the most important United States acrylics are shown in Figure 1. The dogbone shape of Orlon suggests production by a dry-spinning method, whereas the practically round cross section of Creslan indicates a wet-spinning technique. Particles of titanium dioxide, which is used as a delustrant, can be observed in both. Fiber fineness, reported by denier (weight in grams of 9000 meters of fiber), varies commercially from the apparel range, 1–6, up to the carpet range, 15–20.

The mechanical properties of the acrylics may best be studied by observing their stress-strain curves in Figure 2. At low stress, all fibers behave similarly but, above one gram per denier, a spread occurs; at the relatively higher stresses Acrilan shows the most, and Orlon the least elongation. Some of the other more important mechanical properties are listed in Table 1. In it are included four fibers produced in the United States, two in Japan, and one each from the United Kingdom, West Germany, and Sweden. Ranges of values are shown in certain instances to allow for varying fiber denier. The most consistent property listed is specific gravity, which only ranges from 1.12 to 1.19. Moisture regain values (explained in Table 1) range from 1.0 to 2.5% and indicate the hydrophobic nature of the acrylic fibers, an important factor in dimensional stability. All of these fibers are very resistant to sunlight, a property which makes them useful in curtains and awnings. Some special, interesting fiber and yarn morphologies are described below, under Tow, Staple, and Yarns.

Table 1. Physical Properties of Some Acrylic Fibers (10)

Property	Acrilan (U.S.A.)	Courtelle (U.K.)	Creslan (U.S.A.)	Dralon (11) (W. Germany)	Exlan (Japan)	Orlon (U.S.A.)	Tacryl (13) (Sweden)	Vonnel (12) (Japan)	Zefran (U.S.A.)
cross section	round to bean- shaped	round	round	dogbone	round	dogbone	round	round to bean- shaped	round
tensile properties									
tenacity, g/den									
dry	2.0-2.7	3.3-3.6	2.7-3.3	2.5-3.2	2.7-4.0	2.2-2.6	2.5-3.5	2.5-3.0	3.5
wet	1.6-2.2	2.4-2.9		2.1-2.7	2.6-3.8	1.8-2.1	2.5-3.5	2.0-2.5	3.1
tensile strength,									
psi	30,000-40,000					32,000-39,000			45,000-51,000
elongation, %									
dry	36-40	40-45	30-40	24-30	30-40	20-28	25-35	30-40	30
wet	44-49	40-45		24-30	36-44	26-34	27-38	35-45	36
tensile strain recovery, ^a									
% from extension	93	87	89			90			92
of 2% (10a)	1.17	1.15		1.14	1.17	1.14	1.10	1.17	1.19 (8)
specific gravity									
moisture regain, ^b									
%	1.5	1.3	1.0		1.3-2.0	1.5	1.2	1.5-1.8	2.5
effect of heat	sticks at 245°C	sticks at 294°C	becomes tacky at 210°C	softens at 235°C	softens at 232°C	sticks at 235°C (8)	sticks at 240°C	sticks at 245°C	sticks at 255°C
effect of sunlight ^c									

^a Ratio of recoverable extension to the total extension impressed on a fiber. (The test used is similar but not identical to ASTM Designation D1774-61T.)
^b Rate of strain: 8.3%/min; stress decay period: 60 sec; stress decay period: 60 sec.
^c Percent of moisture in a material that is in equilibrium with the atmosphere under standard conditions (70°F and 65% rh).
^d All fibers are very resistant to sunlight.

Of additional interest is the glass transition exhibited by acrylics. When they are heated above the 60–90°C range, they change from an elastic to a viscoelastic state (14). Special advantage is taken of this property in producing high-bulk yarn (see Tow, Staple and Yarns, p. 325).

The flammability of acrylic fibers is of the same general character as is found in other commonly used textile fibers, such as cotton, rayon, and acetate (American Association of Textile Chemists and Colorists (AATCC) Standard Test Method 33-52 or American Society for Testing Materials (ASTM) Method D1230-52T). Acrylics have the unusual property of becoming practically fireproof when they are heated above 160°C in air for prolonged periods (15). The fiber turns black and loses about 60% of its fabric tenacity, yet it may even be placed in a Bunsen flame without further degradation.

Chemical and Biological Properties. In general, all acrylics are resistant to ordinary chemicals, and this makes them particularly useful in work clothing. The acrylics are, however, readily degraded by hot, concentrated alkalis. Chemical and biological properties are summarized in Table 2.

Table 2. Chemical and Biological Properties of Acrylic Fibers

Agent	Effect
age	negligible
acids, inorganic	
weak	little effect
strong	may swell; will dissolve in concentrated HNO ₃ or H ₂ SO ₄
alkalies	
weak	little effect
strong	degraded by hot, concentrated alkalis
organic solvents	negligible for common solvents
oxidizing agents	little effect
insects	negligible
microorganisms	negligible

The acrylics as a class are very resistant to insects and to microbiological attack. Moth and carpet beetle larvae, for example, have virtually no effect on Acrilan (16). None of the fibers are weakened by mold or mildew.

Fiber Analysis and Identification. The composition of the fiber polymers may be determined by a combination of chemical and physical means. An elemental analysis is usually combined with an investigation of ultraviolet and infrared characteristics. Molecular weight may be determined conveniently by measurement of the intrinsic viscosity from dilute solutions of fiber in dimethylformamide.

In a fiber identification scheme which includes the acrylics as well as other fibers, the American Society for Testing Materials uses a combination of microscopic, staining, solubility, and refractive index properties (17). Recently, standard infrared spectral diagrams for Acrilan, Acrilan 16, Orlon 42, Creslan, Zefran, and for the modacrylics Dynel and Verel have been established, and a proposal has been made to add these to the standard method (18).

One producer differentiates between acrylic fibers by first narrowing the possibilities by microscopic observation of the cross sections. Further checking is done by comparison of the results of staining and of reaction with certain chemicals with

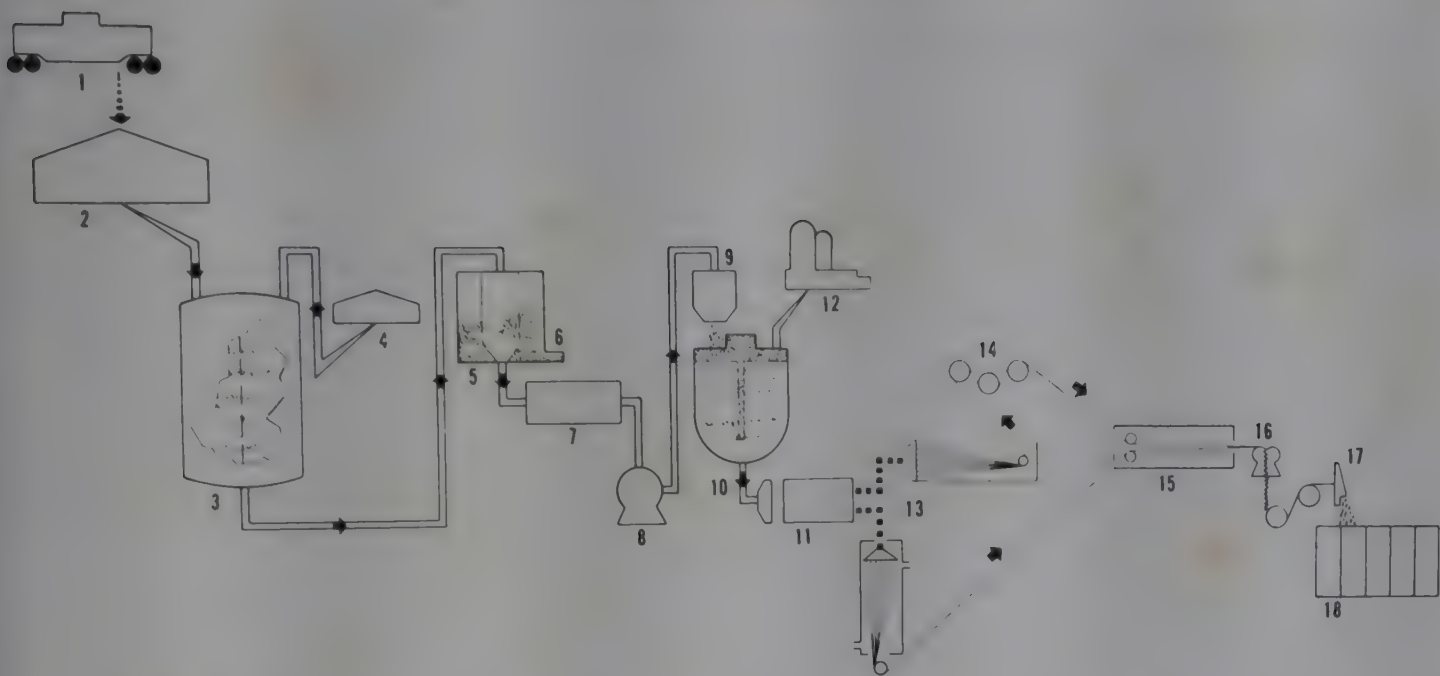


Fig. 3. Manufacture of acrylic fibers. (1) Acrylonitrile; (2) tank farm; (3) polymerizer; (4) added chemicals; (5) centrifuge; (6) waste liquid; (7) dried polymer; (8) grinding; (9) polymer storage; (10) dissolver; (11) filter; (12) solvent plant; (13) spinneret; (14) roller dryer; (15) additional treatment; (16) crimper; (17) cutter; (18) acrylic fiber bale.

the results obtained with properly identified fibers (19). In this method, the cross section is classified as irregular, dogbone, or round. Still further identification is made by staining the fiber with selected acid and direct dyes and reacting with boiling *m*-cresol and boiling formic acid. Other recent methods of identification are based on a combination of solubility, staining, and color reactions (20), and polarized-light microscopy (21).

MANUFACTURE

Acrylonitrile (qv) is the chief raw material for the acrylic fibers. It is a colorless liquid which is easily handled in most of the standard unit processes. Although it is capable of rapid autopolymerization, molecular oxygen is an effective inhibitor so that there are no extraordinary storage problems. It is completely miscible with many organic solvents and appreciably soluble in water. Figure 3 is a flow diagram for the manufacture of acrylic fibers; it shows that the main steps are: polymerizing the acrylonitrile, dissolving the polymer, spinning, and aftertreating.

Polymerization. Various methods used in acrylonitrile polymerization and current ideas on the mechanisms involved are described in an article by W. M. Thomas (22).

The preferred methods of polymerization are solution or dispersion in aqueous media. An activator and a catalyst are used to stimulate the polymerization. The following procedure is based on one of many U.S. patents on the subject (U.S. Patent 2,628,223 (Feb. 10, 1953), J. C. Richards (to Du Pont)): A reaction kettle charged with 1870 parts of water was heated to 44°C. The following reactants were then added:

- 120.0 parts acrylonitrile
- 0.6 part ammonium perdisulfate (0.5% based on the monomer)
- 1.2 parts sodium metabisulfite (1.0% based on the monomer)
- and enough 2*N* sulfuric acid to bring the pH of the mixture to 3.2.

After 45 minutes of batch reaction, the various reactants were metered-in to the polymerizer at rates adjusted to keep the concentration of the reactants constant at the above ratios throughout the reaction. As the additional reactants were added to the kettle, the slurry of polymer was allowed to overflow and was continuously filtered.

It is probable that a free radical $[\text{SO}_4^{\cdot-}]$ is formed by the oxidation of sodium bisulfite by ammonium perdisulfate, which then, either by itself or after reacting with water to form free $[\text{HO}\cdot]$ radicals, adds to and activates the monomer. Other redox activator combinations are $\text{HClO}_3 + \text{H}_2\text{SO}_3$ (23) and $\text{H}_2\text{O}_2 + \text{FeSO}_4 + \text{H}^+$ (24). Recently, the sodium alkoxides have been used as initiators (25).

To improve the dyeability of the fiber, to produce more workable spinning solutions, and for other reasons, acrylonitrile is copolymerized with other monomers. A survey of the patent literature has disclosed many possible comonomers. Some of these have been classified into chemical types and are presented in Table 3.

Table 3. Typical Monomers Copolymerizable with Acrylonitrile (26)

1. <i>Hydrocarbons</i>	6. <i>Amides</i>
styrene	acrylamide
α -methylstyrene	<i>N</i> -dimethylacrylamide
isobutylene	<i>N</i> -dimethylaminopropylacrylamide
2. <i>Alcohols</i>	<i>N</i> -(2-hydroxyethyl)acrylamide
allyl alcohol	7. <i>Acids (or their salts)</i>
methallyl alcohol	acrylic acid
α -hydroxymethylacrylonitrile	methacrylic acid
allyloxyethanol	itaconic acid
3. <i>Ethers</i>	vinylbenzenesulfonic acid
vinyl methyl ether	8. <i>Ketones</i>
allyl ethers of amino alcohols	vinyl methyl ketone
vinyl ethers of amino alcohols	α -acetoxystyrene
allyl glycidyl ether	9. <i>Acrylates</i>
4. <i>Halides</i>	methyl acrylate
vinyl chloride	methyl methacrylate
vinylidene chloride	<i>N</i> -dimethylaminoethyl acrylate
5. <i>Amines</i>	methyl α -acetaminoacrylate
2-vinylpyridine	methoxyethyl acrylate
2-methyl-5-vinylpyridine	methyl α -chloroacrylate
allyldimethylamine	10. <i>Vinyl esters</i>
2-vinylquinoline	vinyl acetate
11. <i>Miscellaneous</i>	vinyl chloroacetate
allylpyridinium chloride	
<i>N</i> -vinyl- <i>N,O</i> -diethylisourea	
vinylidene cyanide	

Mayo and Walling (27) have written an excellent review of the general subject of copolymerization and Alfrey, Bohrer, and Mark (28) have written a book on further aspects of the general subject. Copolymerization as applied to acrylonitrile has been reported in a recent book by American Cyanamid (29). When acrylonitrile and another monomer start to polymerize together, the two monomers ordinarily enter into the copolymer at different rates. The copolymer thereby becomes richer in the more reactive monomer. In a simple batch reaction, this would mean that the com-

position of the copolymer would change continuously. In fiber use it is obviously important for the copolymer to have a consistent composition and this can be achieved conveniently if an additional feed of the more reactive component is fed continuously into the polymerization reactor. In order to obtain a copolymer of the desired composition, it is necessary to know the “reactivity ratios” of the monomers involved. If M_1 and M_2 are the two monomers, the reactivity ratios r_1 and r_2 may be expressed as

$$r_1 = \frac{k_{11}}{k_{12}}, \qquad r_2 = \frac{k_{22}}{k_{21}}$$

where k_{11} = rate constant for the reaction between a copolymer chain ending in M_1 and an M_1 monomer, k_{12} = rate constant for the reaction between a copolymer chain ending in M_1 and an M_2 monomer, k_{22} and k_{21} are the rate constants for the reactions of a copolymer chain ending in M_2 with monomers M_2 and M_1 , respectively.

Some of the reactivity ratios of acrylonitrile (M_1) with comonomer (M_2) are shown in Table 4.

Table 4. Reactivity Ratios of Acrylonitrile (M_1) with Comonomers (M_2) (30)

M_2	r_1	r_2
allyl chloride	3.0 ± 0.2	0.5 ± 0.01
vinyl acetate	4.05 ± 0.3	0.061 ± 0.013
vinyl formate	3.0 ± 0.05	0.04 ± 0.005
vinyl chloride	3.28 ± 0.06	0.02 ± 0.02
vinyl ethyl ether	5	0
methyl acrylate	0.67 ± 0.01	1.26 ± 0.1
methyl methacrylate	0.15 ± 0.07	1.2 ± 0.14

The following equation can be used to calculate the monomer composition required to make a copolymer of acrylonitrile of definite composition:

$$C = \frac{P - 1 + \sqrt{(1 - P^2 + 4Pr_1r_2)}}{2r_1}$$

where C = mole ratio of M_1 to M_2 charged, P = mole ratio of M_1 to M_2 in copolymer.

Terpolymers may also be used to advantage. One patent discloses that approximately 91% acrylonitrile, 4% methyl acrylate, and 5% 2-methyl-5-vinylpyridine may be used to produce a terpolymer soluble in dimethylformamide and with improved dyeing properties (31). Other terpolymer compositions which include acrylonitrile as the predominant monomer are combinations of vinyl acetate and 2-methyl-5-vinylpyridine (32), vinylpyridine and allyl or methallyl alcohol (33), vinylpyridine and styrene, vinyl acetate or some acrylate (34), and acrylamide and an alkylvinylpyridine (35).

Either batch or continuous polymerization may be used. In the batch process reactants are added all at once or over a period of time and the reaction is carried to some substantial degree of completion, whereupon the product is drawn off and the cycle begins over again. In a continuous polymerization process the reactants are continually metered into a reactor with simultaneous withdrawal of product. A blanket of nitrogen, other inert gas, or refluxing monomer over the reactants prevents oxygen from inhibiting the polymerization.

The polymer is insoluble in the aqueous medium and is separated from it by centrifuging. It is then dried, ground, and stored, ready to be dissolved in a suitable solvent to form the spinning dope. Unreacted monomers in the aqueous filtrate may be recycled.

Solvents. As stated earlier, one of the chief barriers in the early development of acrylic fibers was the lack of suitable spinning solvents. (The main function of a polyacrylonitrile solvent is to break the hydrogen bonds so that the individual polymer chains are free to dissolve.) Solution of polyacrylonitrile and its copolymers now is accomplished predominantly by three types of solvents: organic, concentrated inorganic salt solutions, and inorganic acids.

The organic solvents, which are strongly polar and are capable of breaking the interchain hydrogen bonds of polyacrylonitrile, were the first ones used for the commercial production of acrylic fibers. Houtz (4) has described some of the early successful organic solvents. Among them were dimethylformamide, dimethyl sulfone, dimethyl sulfoxide, adiponitrile, and methylenedithiocyanate. Some of the later solvents used were dimethylacetamide (36), mixtures of ethylene sulfite and organic amides (37), and ethylene carbonate (38).

The earliest hydrotropic salt solutions of the polymer (3) did not result in a commercially acceptable process because the polymer could not be recovered in proper structural form from the solvent. However, it was subsequently found that by keeping the spinning bath below 10°C, the structure improved and the process became more operable (39). Thus, a 15% solution of a copolymer (containing at least 85% polyacrylonitrile) was prepared by the use of a 55% aqueous solution of sodium thiocyanate as the solvent. The polymer solution was heated to 60°C and spun into a water bath held at less than 10°C.

Another development was the use of salt mixtures to retain practical dope viscosities at spinning temperatures in the range of 0–45°C. It was possible on the basis of this study to draw up a lyotropic series for polyacrylonitrile, showing the approximate order in which salts dissolve the polymer as shown in Table 5 (40). Each cation listed in the table forms a solvent salt with the anions at equal or higher levels in the table, and forms nonsolvent salts with anions lower in the table. By judicious addition of the proper amount of nonsolvent salt to a solvent salt solution of the polymer, lower spinning dope viscosities are possible. Thus, a 60% ZnCl_2 solution of polyacrylonitrile

Table 5. Lyotropic Series for Polyacrylonitrile

Cations in increasing order of effectiveness	Anions in decreasing order of effectiveness	Cations in increasing order of effectiveness	Anions in decreasing order of effectiveness
K^+	SCN^-	Ga^{3+}	Cl^-
Fe^{3+}		Sb^{3+}	
Pb^{2+}		In^{3+}	
NH_4^+		Tl^{3+}	
Cd^{2+}		Sn^{4+}	
Al^{3+}	I^-	Zn^{2+}	NO_3^-
Na^+		Ag^+	
Ba^{2+}		Ni^{2+}	
Ca^{2+}	Br^-	Co^{2+}	
Li^+		Mn^{2+}	SO_4^-
Mg^{2+}			

has a viscosity of 78 poises at 30°C, but a 45% ZnCl_2 /15% MgCl_2 solution has a viscosity of 42.

P. Halbig found that 68% HNO_3 containing urea was a satisfactory solvent for preparing polyacrylonitrile spinning dopes (41).

By whatever means of dissolving used, a pigment such as titanium dioxide may be thoroughly mixed in with the dope as a delustrant. The spinning dope is then filtered and stored preparatory to the spinning operation.

Wet Spinning. The degassed and filtered spinning dope, which may contain 10–30% polymer in solution, is forced by metering pumps through spinnerets having from 1000 to 12,000 holes. Hole diameters may vary from 2.5 to 4 mils in diameter (42). As the dope leaves the holes it enters a spin bath where the solvent diffuses from the filaments.

Wide ranges in spin bath composition have been used commercially. Naturally, the spin bath will contain some solvent; a low concentration of solvent promotes rapid coagulation but may favor the formation of a skin through which solvent must subsequently be extracted. Concentration is usually adjusted to obtain the structure desired. Other factors of prime importance in spin baths are temperature, time of immersion, and degree of stretching of the fiber. The spin-bath liquid must be a nonsolvent for polymer and yet capable of extracting solvent from the polymer solution (dope) as it emerges from the spinneret holes. The use of chelating agents to enhance the removal of salts from the coagulated polymer, when the polymer has been dissolved in concentrated salt solution, has been reported (43). For recovery, solvent and nonsolvent must be separated by distillation, freezing, or other means. Many substances have been mentioned in patents for use in spin baths: water, alcohols, glycerol, salt solutions, kerosene, xylenes, and glycols.

The coagulated fiber emerging from the spin bath is a highly swollen gel, containing both the dope solvents and spin-bath nonsolvent. In subsequent steps, the fiber is washed free of solvent, stretched 300–1000% to bring about molecular orientation in the direction of the fiber axis, and dried to remove water and to collapse the gel structure into a continuous phase. In some cases, washing and orientation are carried out simultaneously. Molecular orientation can readily be shown by x-ray diffraction. X-ray diagrams of an acrylic fiber, before and after stretching, are shown in Figure 4.

Since the fiber is highly swollen prior to drying, water-soluble and water-dispersed additives can be added and will penetrate the fiber to a varying degree, depending on the amount of swelling of the fiber and other conditions. Under certain conditions of drying, the swollen structure collapses to nearly the density of compression-molded polymer. Providing that all steps of the treatment are properly designed, the collapsed structure is permanent. An example of such a system is given in a patent which describes how the dye receptivity of a polyacrylonitrile fiber is increased by subjecting it "while it is in an aquagel condition to an aqueous solution of polyvinylpyrrolidone" (44). Another procedure is to dye the fiber while it is in the aquagel state by passing it through an aqueous dyebath (45). In one spinning variation, the polymer solution is extruded through the spinneret into an air gap before passing into a series of coagulating baths (46).

Dry Spinning. The dry-spinning process for making polyacrylonitrile yarn is comparable to that for acetate fiber (qv) but nevertheless is different in certain respects. Acetate is spun from a solution in a low-boiling-point solvent (acetone) and essentially all the solvent is vaporized in a drying tower before the product is col-

lected in final package form from the spinning operation. Acrylic fiber is spun from a solvent of much higher boiling point and hence lower evaporation rate. It does not appear to be practical to remove all of the solvent in the tower itself. Therefore, the fiber emerging from the tower normally contains from 10 to 25% of solvent, which is extracted with hot water. Another basic difference from acetate is that the fiber must be oriented by stretching to develop desirable fiber properties as described under Wet Spinning above. In some cases, washing and stretching are done simultaneously.

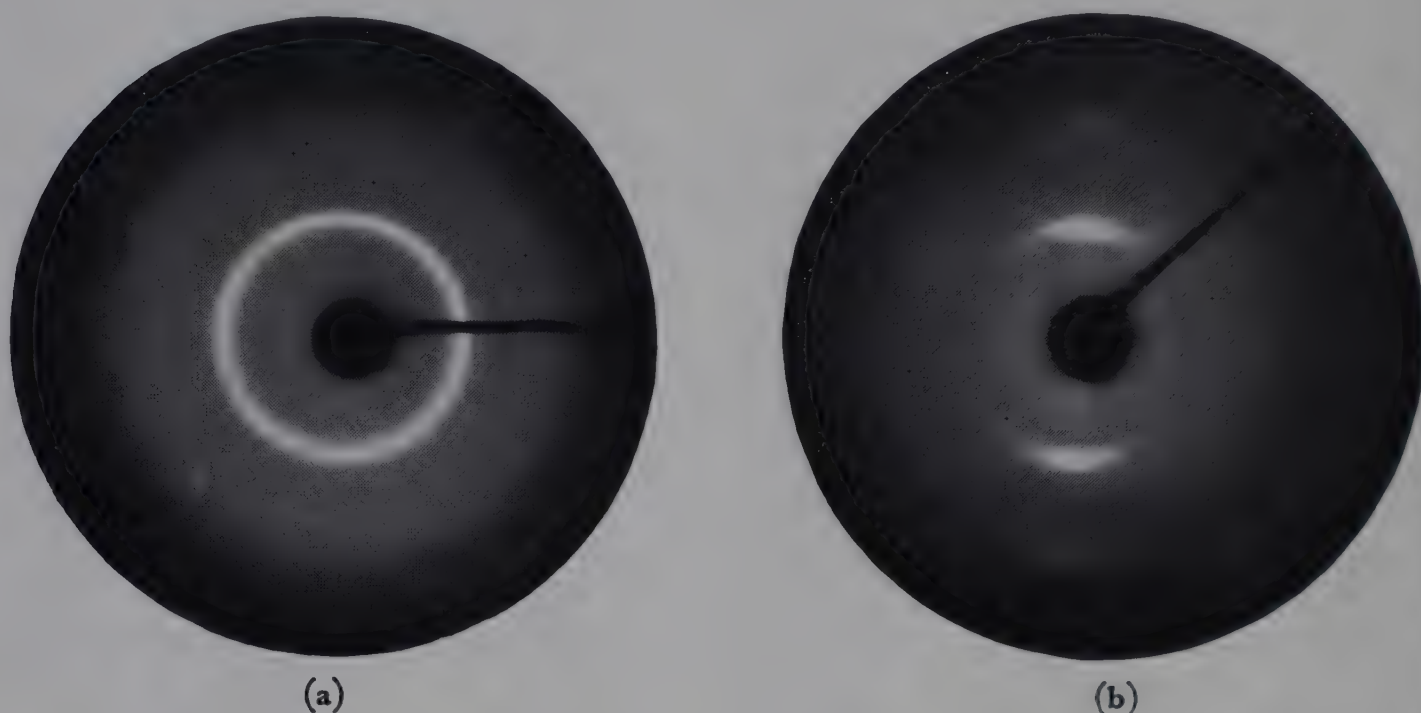


Fig. 4. X-ray diffraction diagrams of Acrilan 16. (a) Before stretching (undrawn). (b) After stretching (drawn).

An interesting variation of the spinning process is one in which composite filaments are formed (47). In one example, a 25% solution of an acrylonitrile homopolymer in dimethylformamide and a 25% solution of a copolymer of 97% acrylonitrile and 3% sodium styrenesulfonate in dimethylformamide were separately prepared and filtered, then pumped to separate inlets of a special spinning chamber. These inlets lead to separate annular rings in the spinneret assembly. The lower edge of separators is positioned near the inside face of the spinneret, this essentially divides the orifices and allows the separate polymer solutions to be spun simultaneously through the same orifice into an evaporative atmosphere.

Finishing. Acrylic fibers, like most fibers, usually require the application of finishes, either before or after drying. The purpose of the finish is to accomplish one or more of the following: (1) reduce static electricity; (2) impart a soft and pliable hand; and (3) lubricate the fiber sufficiently so that it can be processed satisfactorily on textile equipment. The finish composition varies according to the properties of the individual acrylic fiber and the particular characteristics the producer wants it to possess. Usually, a finish will be a mixture consisting of an antistat, a softener, and a lubricating agent to control good fiber-to-fiber and fiber-to-metal (or to other surface) properties. The fiber is then ready for further processing, such as drying (if not previously dried), crimping, cutting, and baling.

Table 6. Types of United States Acrylic Fiber (July, 1961) (49)

Fiber	Type	Denier	Form ^a	Staple length, in.	Luster ^b	Comments
Acrilan (Chemstrand)	regular	2-15	S, T	1 $\frac{9}{16}$ -6	B, D	
	16	1-15	S, T	1 $\frac{9}{16}$ -6	B, D	
	solution-dyed	2.5-3	S, T	1 $\frac{1}{4}$ -4 $\frac{1}{2}$	B	
	FF	6.5	S	2 $\frac{1}{8}$	D	for fiberfill (50), used for stuffing pillows
	BB	5.0	S	2 $\frac{1}{2}$	D	for blanket blend (50)
	77	3	S	1-2 $\frac{1}{2}$	B	Acrilan 16, used for liners; limited cotton system
	88	3	S	1 $\frac{1}{2}$ -3	D	for woolen system
Creslan (American Cyanamid)	89	5	S	1 $\frac{1}{2}$ -3	D	for woolen system
	regular	2-15	S	1 $\frac{1}{2}$ -4 $\frac{1}{2}$	B, D	
	WM	4 (av)	S		B, D	blend of deniers for woolen spinning system
Orlon (Du Pont)	BC	2, 3	S	1 $\frac{1}{2}$	D	for blending with the celluloseics
	42	2-10	S, T	1 $\frac{1}{4}$ -4 $\frac{1}{2}$	B, D	
	38	3 (av)	S	1 $\frac{1}{4}$	B, D	mixture of deniers for pile-fabric trade
	39	4.2 (av)	S	varies	D	blend of deniers for woolen system
	39A ^c	2.5 (av)				
	39B ^c	6.5 (av)				
	36		S	3-4	D	carpet staple
	44	3-6	S, T	1 $\frac{1}{2}$ -3	D	acid-dyeable fiber
	72	1.5	S	1 $\frac{1}{2}$	D	whitened blending staple with cotton
	75	2.5	S	1 $\frac{1}{2}$	D	for cotton/rayon system
Zefran (Dow)	21	3-6	S, T	3 $\frac{3}{4}$ (av)	D	bicomponent fiber, used largely in sweaters
	Orlon Sayelle					
	regular	2-6	S		B, D	
	W-2	2.5 (av)	S		B, D	blend for woolen system
	W-4	4.5 (av)	S		B, D	blend for woolen system

^a S = staple, T = tow. ^b B = bright, D = semidull. ^c Same as type 39 except for denier.

Tow, Staple, and Yarns. In general, filament yarns have a silklike hand, whereas staple fiber feels like wool. Very little continuous-filament yarn is produced at the present time.

The brand names for the acrylics are no longer limited to a specific form; there are now many variations, depending on the special end use the producers have in mind. The multitude of different available forms of American acrylics can be seen in Table 6, ranging from low denier and short length for the cotton spinning system, through the medium denier and longer staple lengths for spinning by the woolen system, to the high-denier staple produced for the carpet industry. From this table, it may be inferred that the production of acrylics is highly competitive and specialized.

Special mention should be made of the high-bulking principle. It is well known that for every high polymer there is a narrow temperature region at which it characteristically changes from a more or less highly resilient state to a viscoelastic state. This is called the glass-transition temperature. If acrylic fiber is heated at 60°C or

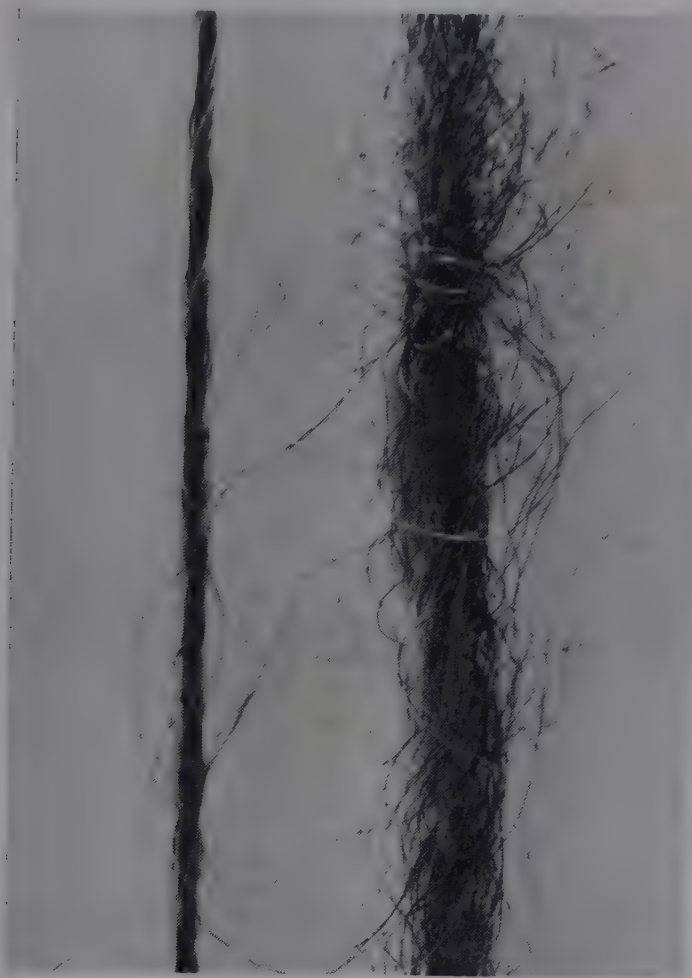


Fig. 5. Yarn of hibulk and regular Acrilan blend before (left) and after (right) relaxation.

above, depending on the individual fiber, stretched 10 to 20%, and then cooled under tension, it is obtained in a metastable state. In this form, the fiber (called "hibulk") is stable at ordinary temperatures and humidities for a long time, and may be processed either alone or preferably in blends with regular acrylic or other fiber, without much change in physical properties (48). When the hibulk fiber in the blended yarn is relaxed in a high-temperature dyebath or by steaming, it shrinks to its original length and thus shortens the entire yarn; this causes the nonshrinking fibers to pucker. Figure 5 shows a $\frac{1}{32}$ s Turbo-converted worsted Acrilan yarn made of hibulk and regular staple, before and after relaxing. The relaxed-yarn count is $\frac{1}{26}$ s. Hibulk Acrilan is commercially available in 2.5-denier tow and staple. Blends of 35 to 50% high-bulk staple seem to be best with respect to yarn shrinkage. Bobek (51) has given a review of some of the more practical manufacturing methods of producing high-bulk yarn in Europe.

Orlon Sayelle was introduced by Du Pont in 1959. Consisting of two bilateral components, it simulates the dual structure of wool. Hicks et al. (52) have summarized work done by the Textile Research Institute in correlating the structural asymmetry of wool fibers with their coiling and crimping nature. Mention was also made of bilateral rayons developed by American Viscose and Du Pont. The physical properties of Orlon Sayelle are quite similar to those of Orlon except that the cross section is acorn-shaped and the elongation is much higher (48 versus 20–28 for Orlon). When heated, one side of the fiber shrinks more than the other, resulting in a high degree of three-dimensional spiral crimp. Another response of the fiber is its behavior on wetting and drying. That side of the fiber which has shrunk more on heating swells more with water and elongates; this decreases the crimp. As the fiber dries,

reecrimping occurs. One way of spinning a bilateral acrylic fiber is described on page 324.

All acrylic fibers appear to be handled relatively satisfactorily on conventional textile machinery. Warp sizes usually consist of thin-boiling modified starches, polyvinyl alcohol, and a lubricant. Extra care must be taken when sizing high-bulk acrylic yarns to prevent the sizing temperature from exceeding the glass-transition temperature.

Because of the bulkiness of the acrylics, special care must also be taken in weaving. For example, acrylics weigh about three-quarters as much as cotton, and attempts to duplicate cotton cloth constructions on regular cotton equipment may cause over-stressing of the loom parts (53). Therefore, finer yarn counts or more loosely constructed fabrics are preferred when acrylics are used to obtain fabrics comparable to rayon, cotton, or wool fabrics; otherwise, the finished fabric may be too compact and stiff.

Dyeing. The polyacrylonitrile fibers in their early development stages were difficult to dye. Later, new techniques to improve dyeability, such as pressure dyeing and the cuprous ion method (54), were developed. In recent years, the dyeability problem has been solved to a large extent by the use of appropriate comonomers in the polymerization of acrylonitrile. Fundamentally, there are four types of comonomers used commercially: (1) the acidic, which contains sulfonic, phosphonic, or carboxylic acid groups and is capable of forming ionic linkages with basic dyestuffs; (2) the basic, which contains amino or pyridine groups capable of forming linkages with acid and direct dyestuffs; (3) the polar, nonionizing type, which has functional groups capable of forming complexes with dyestuffs; and (4) others, including hydrocarbons, which do not of themselves provide dye-reactive groups but which modify the fiber structure to increase the availability of dye sites. A list of some of these comonomers has already been given in Table 3 (see p. 320).

Another means for increasing the affinity of polyacrylonitrile fibers for dyestuffs has been found in the addition to the polymer of hydrophilic groups in the form of epoxy groups (55). This has been accomplished by treating the copolymer with a peracid or other oxidant before spinning.

Many effective external dyeing assistants have also been reported. Among these are urea (56) and quaternary ammonium compounds (57).

Table 7 summarizes the dyeability of some of the United States acrylic fibers. (Only those classes of dyes which are commonly used commercially have been included.) Because of the differential dye affinities of regular Acrilan and Acrilan 16, these two fibers can be cross-dyed. The same is true of Orlon 42 and Orlon 44.

Dope Pigmentation. An alternate way to solve the dyeing problem internally is to incorporate pigment dispersions into the spinning dope to produce solution-dyed yarns. The pigments employed have no affinity for the fiber; the excellent fastness properties thus obtained are due to the inert nature of the colors rather than to a chemical linkage with the fiber. The types of pigments found to be most useful are water- and solvent-insoluble; these include the insoluble azo, anthraquinone, vat, phthalocyanine, and some miscellaneous dyestuffs, carbon black, and certain inorganic pigments. Titanium dioxide is used to produce a delustered or dull appearance. Whereas the properties of the organic dyestuffs have been compiled by Vesce (59), the use of pigments in textiles is discussed by Jones (60). Choice of pigment type will depend on the particular process used in manufacturing the acrylic fiber. The

small particle size (below one micron) causes difficulty in wetting out. The pigment particles are sometimes coated with polymers as an aid in the prevention of agglomerates. The pigment content in the final fiber is normally 5% or below, depending upon shade desired and color strength.

Table 7. Dyeability of Some Acrylic Fibers (58)

Fiber	Dyeability
Acrilan (Chemstrand)	type 1656 takes disperse, basic, acid, acid metalized, neutral premetalized, chrome, and naphthol dyes; type 16, basic and disperse dyes only
Creslan (American Cyanamid)	excellent fastness with acid (premetalized), chrome, direct, acetate, and basic; also vat, sulfur, and naphthol used
Orlon (Du Pont)	dyed with cationic, disperse, acid (copper technique), and selected vat and naphthol dyes (NOTE: Orlon 44 is dyeable with acid dyes)
Zefran (Dow)	dyed with vat, naphthol, or sulfur; aftertreated with direct and neutral premetalized dyes

Solution-dyed Acrilan is commercially available in red, yellow, blue, green, gray, brown, old gold, beige, and black. Orlon may be obtained in black. Prices of the solution-dyed acrylics range from about 10¢ per pound above regular price for the light colors to about 20¢ per pound above, for the dark colors. The manifold outdoor uses for the solution-dyed acrylics include awnings, tarpaulins, lawn furniture, and covers for boats. Some of the apparel uses are swim wear, slacks, suitings, half-hose, and jersey. The solution-dyed acrylics may be blended with stock-dyed, solution-dyed, or undyed fibers of acrylics or other fibers. Cross-dyeing effects may be obtained in blends containing solution-dyed acrylics.

Dow Chemical Company is now producing Zefkrome, a producer-colored acrylic chemically related to Zefran, its parent fiber. Zefkrome, for use especially in the double-knit trade, will be available as staple in 2, 3, 6, and 10 deniers. Initially, it will be supplied in red, blue, green, gold, brown, black, beige, and natural white; the coloring procedure differs from solution dyeing (80).

ECONOMIC ASPECTS

Certain worldwide trends have caused sharp increases in the production of man-made fibers in recent years (61). World population is rapidly increasing, sheep-to-people ratios are declining steadily, cotton crops remain unpredictable, and there are shortages of land suitable for growing other fiber crops. Nevertheless, increasing standards of living are creating greater demands for fiber products.

There are also trends within the fiber industry. In the United States during the period from 1930 to 1950, rayon output increased tenfold; since 1950, rayon output has been fairly constant at about 1.25 billion pounds per year. By comparison, the most important of the synthetic fibers have increased from 38 million pounds in 1945 to 670 million pounds in 1960: nylons, 430 million; polyesters, 100 million; and acrylics, 140 million pounds. Figure 6 (62-64) shows the production of noncellulosic fibers in the United States from 1950 to 1960 with a prediction to 1965 (62). It is seen that the acrylics now amount to about one-fifth of the total noncellulosic market. A growth rate for the acrylics about equal to that of the polyamides over the next five years has been predicted.

Table 8. Selected List of World Producers of Acrylic Fibers and Their Trade Names

Country and location	Producer	Fiber trade name	Type ^a	Estimated 1961 capacity, million lb/year
Belgium Tubize	"Fabelta" (Division of S.A. Union Chimique)	Acribel	S	
Canada Maitland, Ont.	Du Pont Company of Canada	Orlon	S	
China, Mainland Shanghai	Shanghai Synthetic Fiber Factory	undecided	S	(pilot plant)
France Calais	Société Courtaulds France	Courtelle	S	11
Colmar, Vénissieux	Société Crylor	Crylor	S, Y	9
Germany (East) Wolfen Krs. Bitterfeld	Veb Filmfabrik Agfa Wolfen	Wolcrylon	S	
Premnitz Krs. Rathenow	Veb Chemiefaserwerk "Friedrich Engels"	Prelana	S	
Germany (West) Dormagen	Farbenfabriken Bayer A.G.	Dralon	S, Y	
Hamburg-Neumünster	Phrix Werke A.G.	Redon	S	
Kelheim/Donau	Süddeutsche Chemiefaser A.G.	Dolan	S	
Hungary Nyergesujfalu	Magyar Viscosa Részvénytársaság	Pannakril		
Italy Porto Marghera	Società ACSA-Applicazioni Chimiche S.p.A.	Leacril	S	13
Japan Nobeoka, Fuji	Asahi Kasei Kogyo KK	Cashmilon	S	16
Hiroshima	Mitsubishi Vonnell KK	Vonnell	S	16
Saidaiji	Nippon Exlan KK	Exlan	S	16
Fikuyama	Nitto Boseki KK	Nitlon	S	(pilot plant)
Iwakuni	Teihin Acryl KK	(undecided)	S	(pilot plant)
Tokushima, Yoshiwara	Toho Rayon KK	Beslon	S	10.4
Nagoya	Toyo Rayon KK	Toraylon	S	(pilot plant)
Netherlands Dordrecht	du Pont de Nemours (Nederland) N.V.	Orlon	S	15
Nijmegen	Kunstzijdesponnerij Nyma N.V.	Nymcrylon Nymkron	S, T S, T	
Poland Lodz	Lodzkie Zaklady Wlokien Sztucznych	Anilana	S	(pilot plant)
Rumania Savinesti	state-owned plant	Rolan	S	
Spain Monzon	Fibracril, S.A.	undecided	S	
Sweden Ljungaverk	Stockholms Superfosfat Fabriks AB	Tacryl	S	
United Kingdom Coleraine (Northern Ireland)	Chemstrand, Ltd.	Acrilan	S	15

(continued)

Table 8 (continued)

Country and location	Producer	Fiber trade name	Type ^a	Estimated 1961 capacity, million lb/year
Coventry (Warwickshire), Grimsby (Lincolnshire)	Courtaulds, Ltd.	Courtelle	S	32
U.S.A.				
Pensacola, Fla.	American Cyanamid Co.	Creslan	S, T	27
Decatur, Ala.	The Chemstrand Corporation	Acrilan, Acrilan- Spectran	S, T	50
Williamsburg, Va.	The Dow Chemical Company, James River Division, Textile Fibers Department	Zefran	S	15
Camden, S.C., Waynesboro, Va.	E. I. du Pont de Nemours & Com- pany, Inc., Textile Fibers De- partment	Orlon, Orlon Sayelle		120
U.S.S.R.				
Kalinin	state-owned plant	Nitron		
Yugoslavia				
Skopje, Macedonia	Acetilen Fiber & Chemical Com- pany	Makrolan	S	

^a S = staple, T = tow, Y = yarn.

Knit sweaters have proved a lucrative market for acrylics and have cut heavily into an area where wool once was foremost. It is believed that sweaters account for about 65% of the total consumption of acrylics. Rugs and carpets are the next most important market.

In 1952, when acrylic fibers were first produced in any significant quantity, the price per pound averaged about \$1.89. In 1954 and 1955, the price had dropped to \$1.45; by 1956 it had reached a low of \$1.19. Following a slow rise to \$1.25 in the summer of 1961, the present (Nov. 1961) price average is \$1.18 lb.

Europe is a good market for man-made fibers and, at present, the fully synthetic fibers show the most rapid growth (65). Of the three leading fiber types, the acrylics are the fastest growing. There is considerable activity in the acrylic field in Japan (66). With the approval of Beslon manufacture by the Toho Rayon Company, the total Japanese capacity for producing acrylic and modacrylic fibers rose to more than 72 million lb/year. There is now a total of five major acrylic producers in Japan and three other companies are making small quantities in pilot plants.

Soviet man-made fiber production, both semisynthetic and fully synthetic, came to 464 million pounds in 1960. Production of Nitron, the only acrylic fiber now being made in the U.S.S.R., is limited (67). Courtaulds of England accepted an order in April, 1959, for a complete acrylic staple fiber plant and process technology, and this should double the Soviet acrylic supply. The Russians are also very active in textile and polymer research.

Table 8 contains a selected listing of United States and foreign producers of acrylic fibers and of their trade names (68). The type of fiber product and the estimated 1961 plant capacities are also given where they are known.

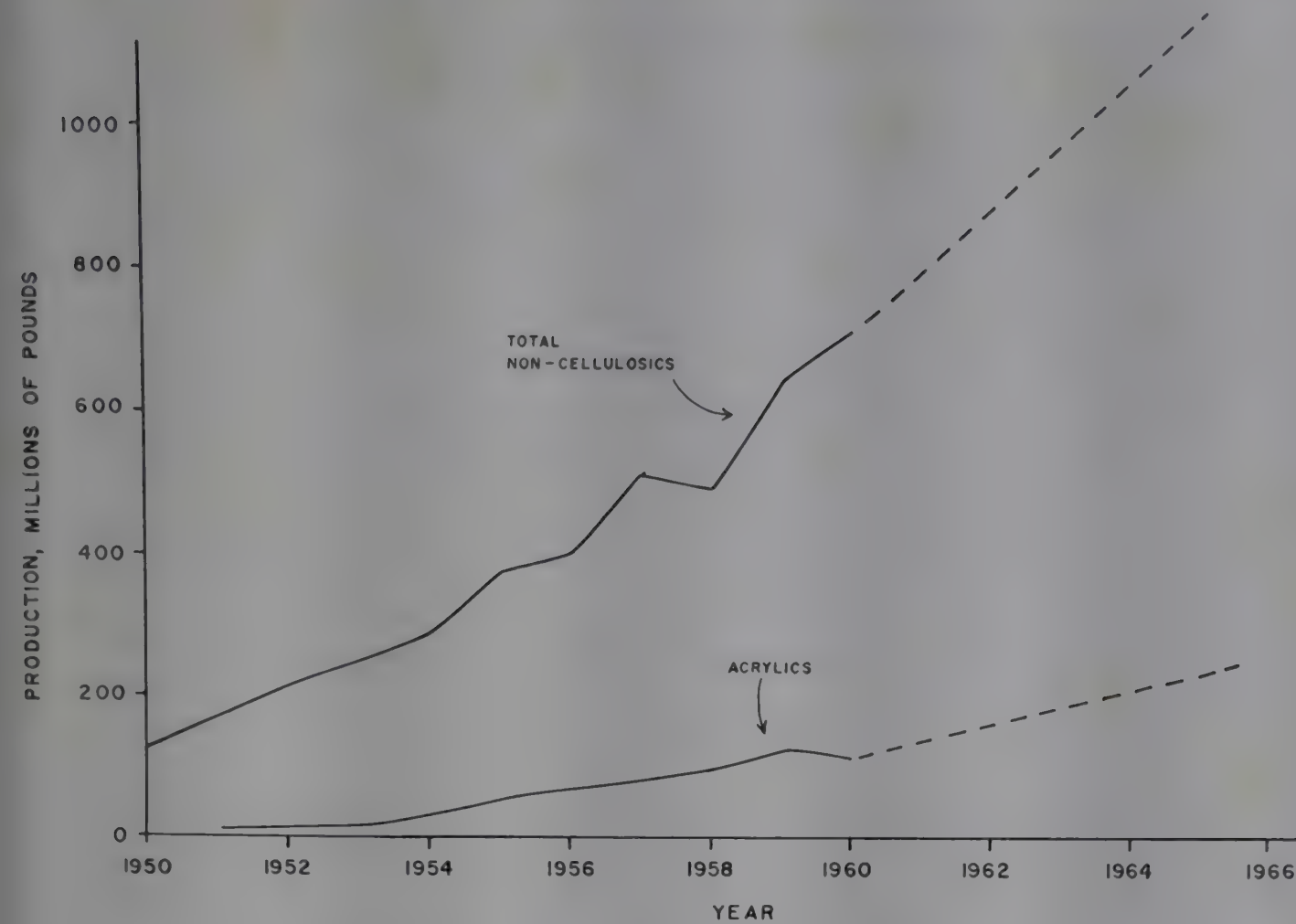


Fig. 6. Production of noncellulosic fibers in the United States.

USES

The wide range of desirable properties of the acrylic fibers have resulted in a variety of end uses. For example, bulkiness permitted the ready acceptance of acrylics in blankets; high resilience has been responsible for their growth in the carpet field; pleat retention during laundering is a big factor in their use in jersey fabrics; acid resistance makes them particularly useful in work clothing. Fabrics of 100% acrylic fiber and those made of blends with fibers are used extensively in four main groups of products—broadwoven apparel, domestic and home furnishings, knit goods, and industrial and miscellaneous items.

In the broadwoven apparel field, the yarn may be processed by means of the cotton, worsted, or woolen spinning systems. Acrylic fabrics, either 100% or blends, are stable to shrinkage. They also exhibit good crease retention and are resistant to wrinkling. Fabrics can also be constructed to take advantage of the bulkiness and high covering power of the acrylic fibers.

The key performance characteristics behind the sales success of acrylics in the carpet field include excellent resilience and crush resistance, excellent stain and soilage resistance, ease of spot removal, good cleanability, good wear life, and appearance durability. In addition acrylic-fiber carpets are mothproof, mildew-resistant, and nonallergenic. Another large market for these fibers is the pile and fleece trade; perhaps one-half (approximately) of the acrylics allotted to this field are converted on the Wildman machine to pile fabrics for rugs, coats, and liners. On the Spring Needle machine, acrylics are converted into liners, fleece, and sleepwear.

In blankets the acrylics provide a soft, luxurious hand, warmth without weight, machine washability and dryability, economy, durability, and dimensional stability. Curtains of acrylic fabrics take advantage of the high resistance of this fiber to the effects of weathering and outdoor exposure; these advantages also apply in the case of awnings. Other important end uses for the acrylic fibers in home furnishings include comforters, pillows, mattress pads, coverlets, novelty throw rugs, and upholstery fabrics.

The major outlet for acrylics is the sweater field, where the special properties of a soft, pleasing hand, retention of knit shape, and resistance to stretch and to attack by moths can be used to advantage. The jersey market for acrylics is growing. In this area, the properties of resistance to stretch, easy launderability with dimensional stability, and quick drying are important.

Industrially, the fiber may be employed where chemical stability and resistance to weathering are needed, for example, in filter cloths, collection bags, tents, tarpaulins, and diaphragm fabrics. Work clothing of acrylic fiber has been worn for unusually long periods in areas where acids caused cotton clothing to deteriorate rapidly.

Modacrylic Fibers

Modacrylic fiber production is growing but at a slower pace than acrylic fiber production. (See Table 9 (67-69) for a selected list of world producers.) At the present time Dynel and Verel are the leading fibers in the United States; Kanekalon in Japan; and Velicren in Italy. In Russia, two modacrylics are in development, Saniv, a 60/40 vinylidene chloride/acrylonitrile copolymer and Kanekalon, a 60/40 acrylonitrile/vinyl chloride copolymer. In 1961 Union Carbide Chemicals Company began limited commercial production of Aeress, a continuous-filament modacrylic. This fiber is known to differ chemically from Dynel, the company's other modacrylic, and is understood to have higher heat resistance (69). Verel is also available in a textured continuous-filament yarn for carpets (70). The unique spectrum of properties

Table 9. Selected List of World Producers of Modacrylics and Their Trade Names

Country and location	Producer	Fiber trade name	Type ^a	Estimated 1961 capacity, million lb/year
Italy				
Cesano Maderno	Società Nazionale Industria Applicazioni Viscosa (SNIA Viscosa)	Velicren	S	
Japan				
Hyogo-ken (Takasago)	Kanekalon KK	Kanekalon	S	16
U.S.A.				
Kingsport, Tenn.	Tennessee Eastman Company	Verel	S, CF	5
South Charleston, W.Va.	Union Carbide Chemicals Company, Textile Fibers Dept.	Dynel	S, T	6-8
		Aeress	CF	
U.S.S.R.				
	state-owned	Kanekalon		
	state-owned	Saniv		

^a S = staple, T = tow, CF = continuous filament.

of the modacrylics has permitted the development of a wide array of products ranging from air filters and anode bags to hats and simulated fur coats.

The manufacturing process for the modacrylics differs from the general process for the acrylics in one main respect: The lower acrylonitrile content permits the use of cheaper and lower-boiling solvents. The first step in manufacture, as for the acrylics, is the controlled polymerization of acrylonitrile with at least one other comonomer. Suitable additives may be included for enhancing certain properties. After dissolving the polymer and additives in the low-boiling solvent, the resultant spinning dope is forced through the holes of spinnerets. The polymer is coagulated by wet- or dry-spinning methods, the filaments are washed and stretched, and the modacrylic fiber is produced as continuous-filament yarn, tow, or staple.

At the present time, not enough published information is available on Aeress, Velicren, or Saniv, but Dynel and Verel will be discussed individually. The physical properties of these two, as well as Kanekalon, are listed in Table 10.

Table 10. Physical Properties of Some Modacrylic Fibers

Property	Dynel	Kanekalon	Verel
cross section	ribbon	ribbon	peanut-shaped
tensile properties			
tenacity, g/den			
dry	2.5-3.3	2.8-3.6	2.5-2.8
wet	2.5-3.3	2.8-3.6	2.4-2.7
elongation, %			
dry	35-38	37-33	33-35
wet	35-38		
specific gravity	1.30	1.28	1.37
moisture regain, %	0.4	0.6-0.7	3.5-4.0
effect of heat	shrinks 1.5-3.5% in dry heat at 120°C for 20 minutes	softening point at 150-160°C	at 130-150°C, tenacity and modulus decrease, elongation increases
effect of sunlight	all fibers are very resistant to sunlight		

DYNEL

Dynel is manufactured by the Union Carbide Chemicals Company and is composed essentially of a 60/40 vinyl chloride/acrylonitrile copolymer. Its predecessor, Vinyon N, was a continuous-filament yarn with about the same composition. Vinyon N was quite susceptible to heat and there was difficulty in producing it by a low-cost, continuous process. But in 1949 the production process was streamlined, improvements were made in the copolymer, and staple fiber was made rather than continuous filament. The new modacrylic was called Dynel.

Properties. Dynel is characterized by good dry and wet strength, dimensional stability, warmth, resilience, rapid drying, high resistance to both combustion and chemical degradation, moth- and mildewproofness, and thermoplasticity. The fiber's physical properties are shown in Table 10 (71-73) and a cross section of the fiber is shown in Figure 7. Stress-strain diagrams for two of the modacrylics are shown in Figure 8 (72,73). One of the differences in physical properties between the presently commercial modacrylics and acrylics is the higher specific gravity of the modacrylics (1.28-1.37), which puts them in the same class with wool in this respect.

The present modacrylics are resistant to ordinary chemicals, partly because of very low moisture regain. Table 11 summarizes some of their important chemical and biological properties.

Table 11. Chemical and Biological Properties of the Modacrylics

Agent	Effect
sulfuric acid, 70%, at 50°C	little
hydrochloric acid, 38%, at 50°C	no effect
nitric acid, 40%, at 50°C	no effect
sodium hydroxide, 50%, at 50°C	little effect
hydrogen peroxide, 30%, room temp.	little effect
organic solvents	negligible for common solvents except acetone
insects	negligible
microorganisms	negligible

Dynel has a high ignition temperature and is self-extinguishing. It has a second-order transition temperature of 80–100°C. Above this temperature its resistance to stress is reduced and the fiber becomes susceptible to penetration and swelling by water, an important consideration in dyeing and finishing.

Manufacture (74). The copolymerization of the vinyl chloride and acrylonitrile monomers comprising the Dynel resin is accomplished by an emulsion process. At the completion of copolymerization, the resultant resin is coagulated, washed, and dried, and emerges as a white, fluffy powder.

The dried resin is then dissolved in acetone and extruded through a multiholed spinneret into an aqueous coagulating bath. After washing, to remove solvent, and application of a finish, it is stretched to from five to 15 times its original length; this process accounts for the final tenacity and elongation characteristics of the fiber. Next, the fiber is annealed or baked by exposing the yarn to hot circulating air. This treatment relieves strains and reduces subsequent shrinkage. Finally, the fiber is crimped, cut, and baled for shipment.

Dynel staple is currently supplied in deniers of 2, 3, 6, 12, 15, and 24, and in staple lengths ranging from 1¼ to 5 in. The fiber is also available in 180,000-total-denier tow. Dynel is produced as standard staple (type 80), high-shrinkage staple (type 83), and carpet fiber (type 97).

Dyeing. Dynel has a high natural affinity for disperse, cationic, and premetalized acid dyes. The disperse dyes are easiest to apply and possess good leveling qualities. They are capable of producing most of the shades desired on Dynel with adequate fastness for most end uses. In the dyeing of heavy shades, sodium sulfate is often added to the dyebath to improve color exhaustion. The cuprous ion method is used in dyeing with acid dyes. Dynel can be solution-dyed, and blond, pewter, gray, brown, charcoal, and black are available. It may also be obtained bright or delustered.

Economic Aspects. In the latter part of 1953, the demand for Dynel made it necessary to increase fiber production. The Vinyon N operation was brought to a close and the manufacturing space was converted for the production of Dynel. This changeover raised fiber output to the level of 5,000,000 pounds per year. Present (1960) capacity is 6–8 million pounds.

When Dynel was introduced to the market in 1949, its price was \$1.25 per pound (75). It rose to \$1.28 in 1952 and remained at that level until 1956, when it dropped

to \$1.05. From 1958 to October 1961, the price of Dynel was \$1.10 and, in October 1961, it was reduced to 75¢ a pound.

Uses. Proper choice of the denier or size of the Dynel fibers used and a choice of spinning systems make it possible to construct fabrics with a wide range of hand. Dynel, alone or in blends, is used in bed and baby blankets, draperies, men's suits and slacks, work clothing, deep pile coats, pile linings and trim, underwear, filter fabrics, paint-roller covers, sail cloth, chemical-resistant clothing, carpets, throw rugs, and as a protective overlay for glass-reinforced plastics.

Special use can be made of Dynel's thermoplasticity (76). The fabric can be placed in a mold, then heated and cooled; it will retain its molded form until reheated. Covers for furniture seats and arm rests, protective packaging for delicate instruments, and men's rain-resistant summer hats are examples of end uses.

VEREL

Verel was announced in March 1956 by Eastman Chemical Products, Inc., a subsidiary of Eastman Kodak Company (77). Tennessee Eastman Company, a corporate associate, developed the fiber and actually produces it. When first available, Verel was supplied as a low-, medium- or high-shrink yarn. There was also a flame-resistant form known as Verel FR. The types now commercially available are shown in the Manufacture section.

Properties. Verel possesses the general physical characteristics of other acrylic and modacrylic fibers, but differs from them in certain respects: It exhibits good whiteness and good flame resistance, and it has a relatively high moisture regain. The physical, chemical, and biological properties of Verel are shown in Tables 10 and 11 and in Figures 7 and 8.



Dynel (type 80)
Courtesy Union Carbide Chemicals Company.



Verel
Courtesy Tennessee Eastman Company.

Fig. 7. Photomicrographs of cross sections of two modacrylic fibers.

Manufacture. The details of Verel manufacture have not been published but the peanut-shaped cross section of the fiber suggests a dry-spinning process. Verel is processed satisfactorily by all the systems of spun-yarn manufacturing and no major changes or modifications in processing are required. No special techniques are needed for winding, warping, and weaving, but warps containing a high percentage of Verel should not be unduly stretched in slashing unless a shrinking or bulking action is desired in the finished fabric.

Three classes of dyes are considered most effective from a standpoint of fastness and economy. They are the neutral-dyeing premetalized dyes, the dispersed acetate dyes, and basic or cationic dyes. Operating temperatures of 180–205°F are sufficient to completely exhaust these dyes over the full shade range (78). Verel is available delustered but not solution-dyed.

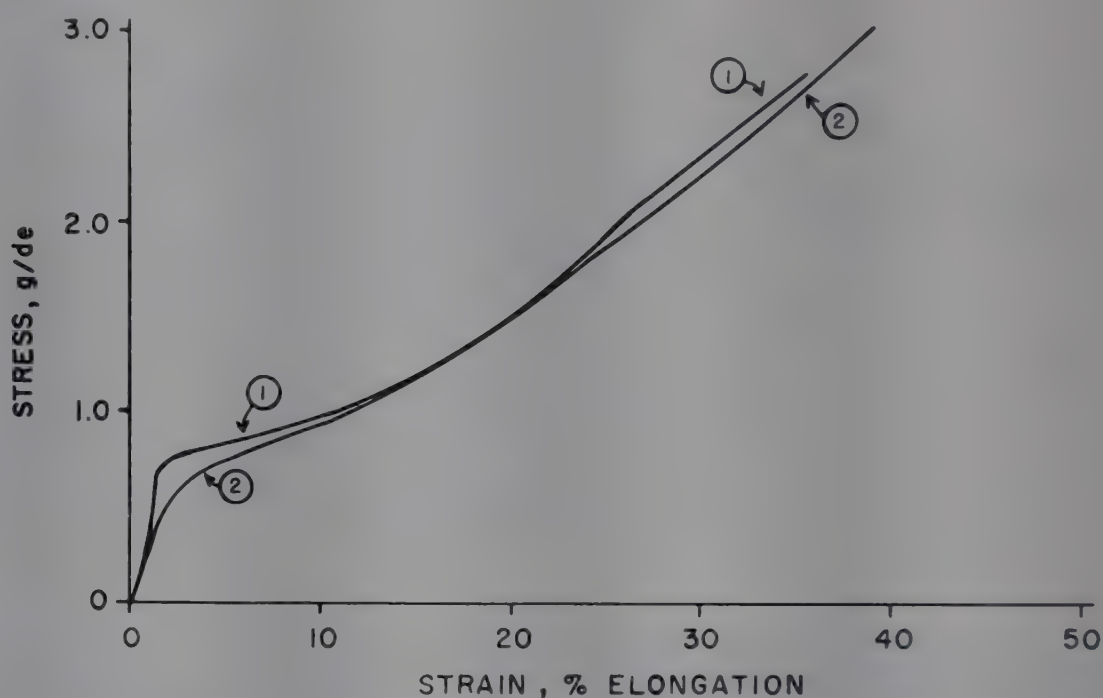


Fig. 8. Stress-strain relationships for some modacrylics. ① Verel (Tennessee Eastman Company). ② Dynel (Union Carbide Chemicals Company).

Verel staple and tow may be obtained in denier sizes from 2.75 to 24. Types A, B, C, D, and HB differ in crimp properties. Type HB, for example, has a very high, very permanent crimp, whereas Type C has a medium crimp which is easily removed. Type F has greater denier and length variation than the other types. Type III is a controlled-shrinkage fiber. Verel continuous-filament yarn for carpets is available in a 2700-denier size.

The price of staple from its inception to 1958 was \$1.10/lb. The price dropped in the following year to \$1.02 and as of November, 1961, is \$0.75/lb.

Uses. Verel, because of its soft hand, whiteness, good flame resistance, and controlled shrinkage, is of considerable interest for making pile-type fabrics, including man-made furs, of both knitted and woven types. Other end uses include trim for cuffs, collars, boots, and shoes, as well as a wide range of liner fabrics. In knit goods the ability to retain a soft hand after repeated laundering and drying qualifies Verel for blending with cotton for sport shirts, undershirts, and children's sleepers. The relatively high moisture regain is particularly valuable when Verel is blended with wool and cotton for socks. Blends containing from 30 to 50% of Verel with wool or cotton give good dimensional stability, a comfortable feeling, and little pilling tendency.

Verel has properties which make it useful in the carpet trade (79). It has adequate crush resistance and good soil resistance, also flame resistance, mildew- and mothproofness, and good dyeing qualities. Verel is available in various staple forms, differing in their carefully controlled levels of crimp.

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ACRYLONITRILE

Acrylonitrile (vinyl cyanide), $\text{CH}_2=\text{CHCN}$, formula weight 53.03, is a colorless liquid with a faintly pungent odor. It was discovered in 1893 by Moureu (1) who prepared it by dehydration of either acrylamide or ethylene cyanohydrin with phosphorus pentoxide.



This very versatile compound was practically unknown until shortly before World War II when the Germans began the development of its copolymers with butadiene for use in oil-resistant rubber. Its manufacture in the United States began in 1940, and expanded very rapidly during the next few years to meet war needs, particularly for nitrile rubber used in self-sealing liners for aircraft fuel tanks. A wide variety of uses has developed since that time, particularly in synthetic fibers, plastics, modified natural fibers, hydrolyzed polymers as polyelectrolytes, and as a chemical intermediate. The rapid growth in acrylonitrile production since 1950 has been due almost entirely to acrylic fibers. Acrylic fibers accounted for over 60% of the U.S. consumption of 229 million pounds in 1960.

The present commercial product is of extremely high purity; impurities other than water are present only in parts per million. The presence of a few tenths of a percent of water is desirable to improve the stability of the product.

Properties

Some of the more important physical properties of acrylonitrile are given below. A more detailed listing with references to the original work is given in reference 2.

Physical Constants.

appearance	colorless liquid												
critical pressure	34.9 atm												
critical temperature	246°C												
density, 20°C	0.8060 g/ml												
25°C	0.8004 g/ml												
dielectric constant (33.5 megacycles)	38												
explosive limits (by volume in air at 25°C)	3.05 to 17.0% ± 0.5%												
flash point	−83.55 ± 0.05°C												
ignition temperature	481°C												
molar refraction (D line)	15.67												
molecular weight	53.06												
odor	faintly pungent												
refractive index, n_D^{25}	−1.3888												
surface tension (24°C)	27.3 dynes/cm												
vapor density (theoretical)	1.83 (air = 1.0)												
vapor pressure	<table><tr><th>mm Hg</th><th>°C</th></tr><tr><td>50</td><td>8.7</td></tr><tr><td>100</td><td>23.6</td></tr><tr><td>250</td><td>45.5</td></tr><tr><td>500</td><td>64.7</td></tr><tr><td>760</td><td>77.3</td></tr></table>	mm Hg	°C	50	8.7	100	23.6	250	45.5	500	64.7	760	77.3
mm Hg	°C												
50	8.7												
100	23.6												
250	45.5												
500	64.7												
760	77.3												

Azeotropes.

	<i>Bp, °C</i>	<i>Acrylonitrile, wt %</i>
benzene	73.3	47
carbon tetrachloride	66.2	21
methanol	61.4	39
isopropyl alcohol	71.7	56
water	71	88

Solubilities. Solubilities of water in acrylonitrile and of acrylonitrile in water, as % in solution, are given below:

Temperature, °C	Water in acrylonitrile	Acrylonitrile in water
0	2.1	7.2
20	3.1	7.35
40	4.8	7.9
60	7.6	9.1

Acrylonitrile is miscible with most common organic solvents including acetone, benzene, carbon tetrachloride, ether, ethyl acetate, ethylene cyanohydrin, methanol, petroleum ether, toluene, xylene, and some kerosenes.

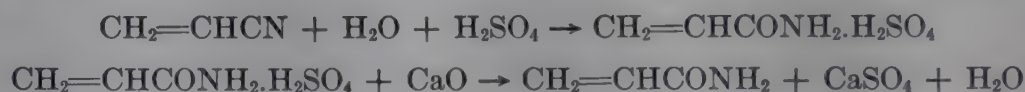
Thermodynamic Data.

entropy (vapor, 25°C, 1 atm)	65.47 cal/(°C) (mole)
free energy of formation (vapor, 25°C)	+45.37 kcal/mole
heat of combustion (liquid, 25°C)	-420.8 kcal/mole
heat of formation (liquid, 25°C)	+36.20 ± 0.13 kcal/mole
heat of vaporization (0-77°C)	7.8 kcal/mole
molar heat capacity (liquid)	26.5 ± 1.5 cal/(°C) (mole)
molar heat capacity (vapor, 77-1000°C, 1 atm)	6.75 ± 33.27 × 10 ⁻³ T - 10.91 × 10 ⁻⁶ T ² cal/(°C) (mole), (1585 kcal/mole)

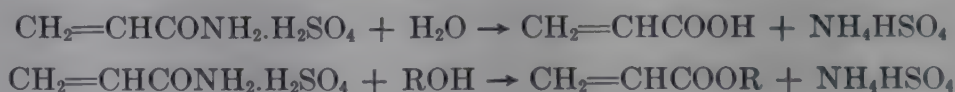
CHEMICAL REACTIONS

Acrylonitrile is a very versatile chemical intermediate. Its reactions may involve the cyano (CN) group alone, the activated double bond (C=C), or both groups. The most important reaction, commercially, is its polymerization. Only a few examples of the major types of reactions are included here. A comprehensive listing of references for reactions reported through 1957 is given in reference 2.

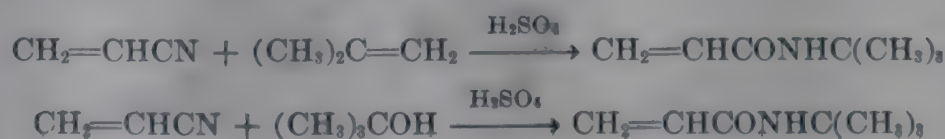
Reactions of the Nitrile Group. Acrylonitrile is hydrated readily at 100°C by 84.5% sulfuric acid (the monohydrate of sulfuric acid, H₂SO₄·H₂O) to produce acrylamide sulfate. Neutralization of the sulfate gives acrylamide (qv), a commercially important, water-soluble monomer (3). (See also Nitriles and isocyanides.)



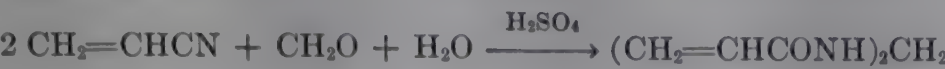
When more dilute sulfuric acid is used, or acrylamide sulfate is heated with water, the product is acrylic acid. Also, the further reaction of acrylamide sulfate with alcohols is a useful method of producing acrylic esters.



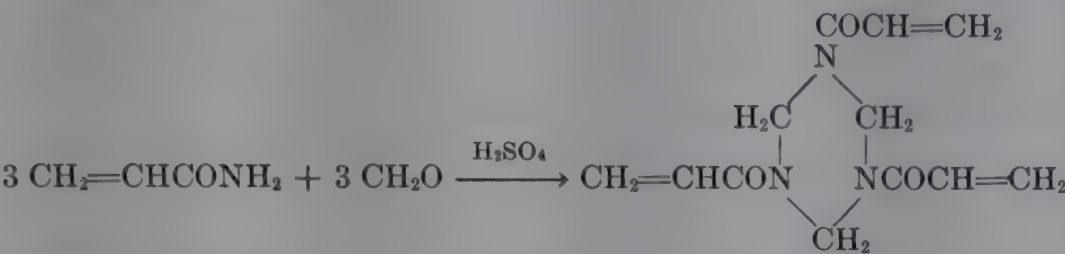
The reaction with an olefin in the presence of concentrated sulfuric acid, followed by hydrolysis of the intermediate, is used to prepare *N*-substituted acrylamides. A similar reaction can be carried out using an alcohol instead of the olefin (4). The preparation of *N*-*tert*-butylacrylamide is an example.



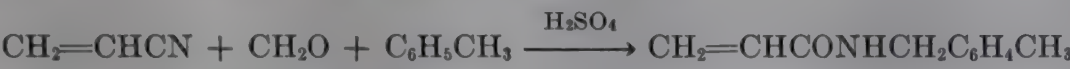
The reaction with formaldehyde and excess 85% sulfuric acid produces *N,N'*-methylenebisacrylamide.



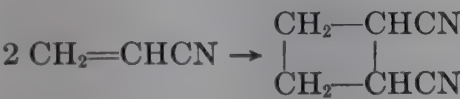
When anhydrous formaldehyde and acrylamide are reacted with a catalytic amount of sulfuric acid, the product is an interesting trifunctional monomer, 1,3,5-triacrylylhexahydro-*s*-triazine.



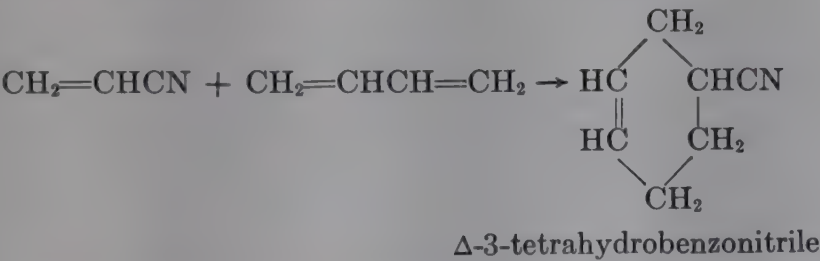
The reaction with an aromatic hydrocarbon and formaldehyde in the presence of sulfuric acid to give good yields of acrylyl derivatives of aminomethylbenzenes has been reported (5). Toluene, for example, gives a para derivative:



Reactions of the Double Bond. Acrylonitrile can be dimerized by heating under pressure at 190–200°C to give 1,2-dicyanocyclobutane. Conversions are low but yields of about 90% have been reported (6).



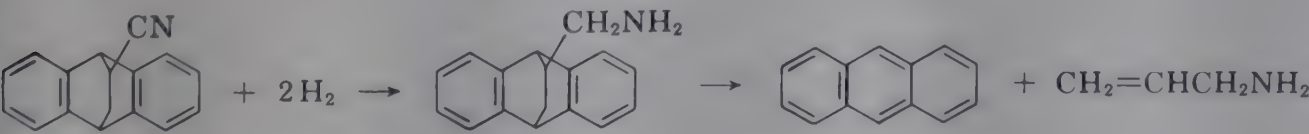
Many examples of Diels-Alder reactions have been reported and yields are usually excellent. The reaction with butadiene is an example.



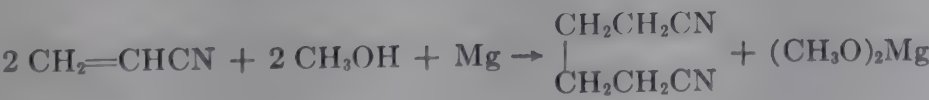
Hydrogenation under mild conditions gives propionitrile which can be further hydrogenated to *n*-propylamine.



The direct hydrogenation to allylamine has not been reported. This can be accomplished, however, by hydrogenating the Diels-Alder adduct with anthracene and thermally cleaving the resulting product.



Reductive coupling—for example, with magnesium and methanol—produces adiponitrile.

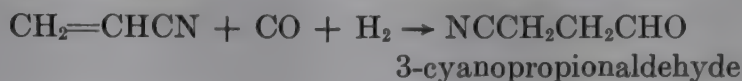


The chlorination of acrylonitrile at low temperature proceeds by addition to yield 2,3-dichloropropionitrile. The reaction is catalyzed by ultraviolet radiation or pyridine. The ultraviolet-catalyzed reaction has been reported to give a 75% yield of this product (7).



The pyridine-catalyzed addition has been reported to give nearly quantitative yields at low conversions. However, at high conversions, the reaction is complicated by dehydrochlorination to 2-chloroacrylonitrile; further addition of chlorine gives 2,2,3-trichloropropionitrile. This further chlorination appears to be catalyzed by hydrogen chloride (8). Vapor phase chlorination over activated carbon gives 2-chloroacrylonitrile directly (9).

The carbonylation of acrylonitrile is the basis for an apparently useful synthetic route to monosodium glutamate (10). (See Amino acids.)

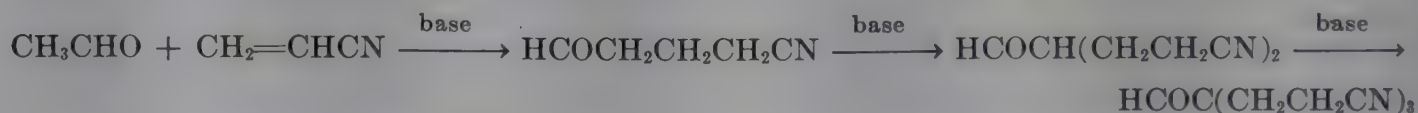


The 3-cyanopropionaldehyde is converted, with hydrogen cyanide and ammonia, to 2-aminoglutaronitrile ($\text{NC}(\text{CH}_2)_2\text{CHNH}_2\text{CN}$), which is then hydrolyzed to glutamic acid.

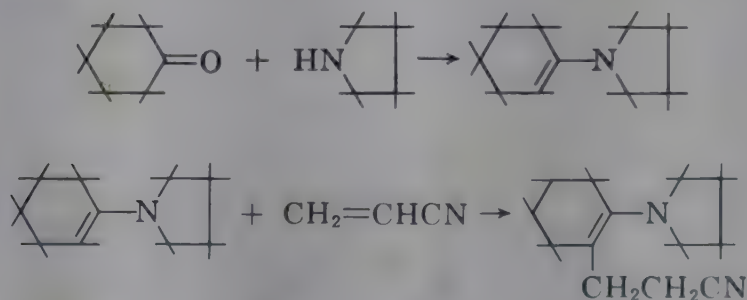
Cyanoethylation (qv) is a term which has been applied to the reactions of acrylonitrile with active hydrogen compounds, thus introducing the cyanoethyl group into the reacting molecule (11). The reaction is usually base-catalyzed. It is given below in general terms. The molecule AH may be a member of many classes of compounds—for example, water, alcohols, ammonia, amines, mercaptans, aldehydes, inorganic acids and their salts, aldehydes, ketones, some esters, and aliphatic nitro compounds.



A cyanoethyl group can be attached directly to carbon if the carbon atom is sufficiently activated. The reaction is often complicated, however, by polycyanoethylation when the carbon atom holds more than one hydrogen atom. For example, a mixture of mono-, di-, and tricyanoethylated derivatives results from the cyanoethylation of acetaldehyde.



Monocyanoethylation of cyclohexanone has been accomplished indirectly by formation of the pyrrolidine enamine prior to cyanoethylation (12).



The cyanoethylated enamine is hydrolyzed readily to the ketonitrile.

The behavior of aliphatic nitro compounds is similar to that of aldehydes and ketones. Other compounds, including esters, amides, nitriles, and sulfones, can be

cianoethylated only if there are two activating groups attached to the carbon atom involved in the cyanoethylation.

The cyanoethylation of aliphatic primary and secondary amines to produce 3-cyanopropylamines can usually be carried out without a catalyst. Primary amines can lead to dicyanoethylation products but the reaction can usually be controlled so that one product is obtained.



Aromatic amines are somewhat less reactive. The cyanoethylation of aniline and its derivatives, leading to $\text{C}_6\text{H}_5\text{NHCH}_2\text{CH}_2\text{CN}$, can be carried out in acetic acid or with a cupric acetate catalyst, however (13).

Cyanoethylation of alcohols produces 3-alkoxypropionitriles: $\text{ROH} \rightarrow \text{ROCH}_2\text{CH}_2\text{CN}$. The reaction requires a basic catalyst and proceeds quite well with primary and secondary alcohols. Tertiary alcohols react much less readily, however. This reaction is the basis for the cyanoethylation of natural polymers such as starch and cellulose.

The cyanoethylation of mercaptans is quite similar to that of alcohols. The reaction with hydrogen sulfide or sodium sulfide to give the dicyanoethyl thioether, $\text{S}(\text{CH}_2\text{CH}_2\text{CN})_2$, and with sodium bisulfite to give the sodium salt of 3-sulfopropionitrile (2-cyanoethanesulfonic acid), $\text{NaO}_3\text{SCH}_2\text{CH}_2\text{CN}$, are other interesting examples of sulfur cyanoethylation.

The cyanoethylation of polymers has received a great deal of study, particularly in the past few years. The reaction which is of greatest interest, the cyanoethylation of cellulose, is a specific case of cyanoethylation of hydroxy compounds. Conditions for controlling this heterogeneous reaction to introduce varying levels of nitrogen have been described. A report on the cyanoethylation of cotton has been issued jointly by the Institute of Textile Technology, American Cyanamid Company, and Monsanto Chemical Company (14). See also under Uses.

Polymerization. Polymerization is by far the most important reaction of acrylonitrile. Polymers, in fact, accounted for more than 95% of the total use in 1960. The vinyl polymerization reaction is usually initiated by "redox" catalysts, but may also be initiated by peroxides, azo compounds, light, high-energy radiation, and strong bases. Acidic catalysts are generally ineffective because of the electron-deficient character of the double bond. (See Acrylic acid and derivatives; Acrylic and mod-acrylic fibers.)

Copolymers with numerous monomers are discussed in the literature. In general, acrylonitrile imparts many unique properties to these materials. Some properties of polyacrylonitrile include hardness, heat and fire resistance, solvent resistance, ability to form oriented fibers and films, reactivity of the nitrile group, and polarity of the nitrile group.

The alkaline hydrolysis of polyacrylonitrile gives a polyelectrolyte which is predominantly a salt of polyacrylic acid. Polymers of this type are used as soil aggregating agents (see Soil chemistry), to control water loss in oil well drilling muds (see Drilling fluids), and as flocculating agents. (See also under Uses.)

Manufacture

Acrylonitrile is currently produced from (1) ethylene cyanohydrin (see Cyanohydrins), (2) acetylene and hydrogen cyanide (see Cyanides), and (3) propylene and

ammonia. In addition, several other possibly useful processes are described in the patent literature.

FROM ETHYLENE CYANOHYDRIN

Ethylene cyanohydrin was the raw material for American Cyanamid's initial production of acrylonitrile. At the present time, however, it is being used by only one major producer (Union Carbide). In pure form ethylene cyanohydrin is a colorless liquid, bp 227–228°C, produced by the reaction of ethylene oxide with hydrogen cyanide.



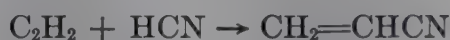
Ethylene cyanohydrin spontaneously decomposes, slowly, into acrylonitrile and water. The decomposition is accelerated by use of a catalyst. The preferred catalysts are alkali metal salts of organic acids, particularly formates (16,17).



The crude product obtained by this process is largely a mixture of acrylonitrile and water with no impurities boiling near acrylonitrile. It can be refined by fractional distillation to give acrylonitrile of high purity.

FROM ACETYLENE AND HYDROGEN CYANIDE

The reaction of acetylene with hydrogen cyanide is utilized in the production of about two-thirds of the acrylonitrile produced in the United States. It is also used by most of the major foreign producers.



The reaction proceeds only in the presence of a catalyst. There are numerous patents, both on processes for the reaction and on purification of the product. References to only a few of the most significant patents are included here.

Liquid Phase Catalysis. The liquid phase, acetylene-based process for acrylonitrile was developed in Germany in the early 1940s. Small plants were operated at

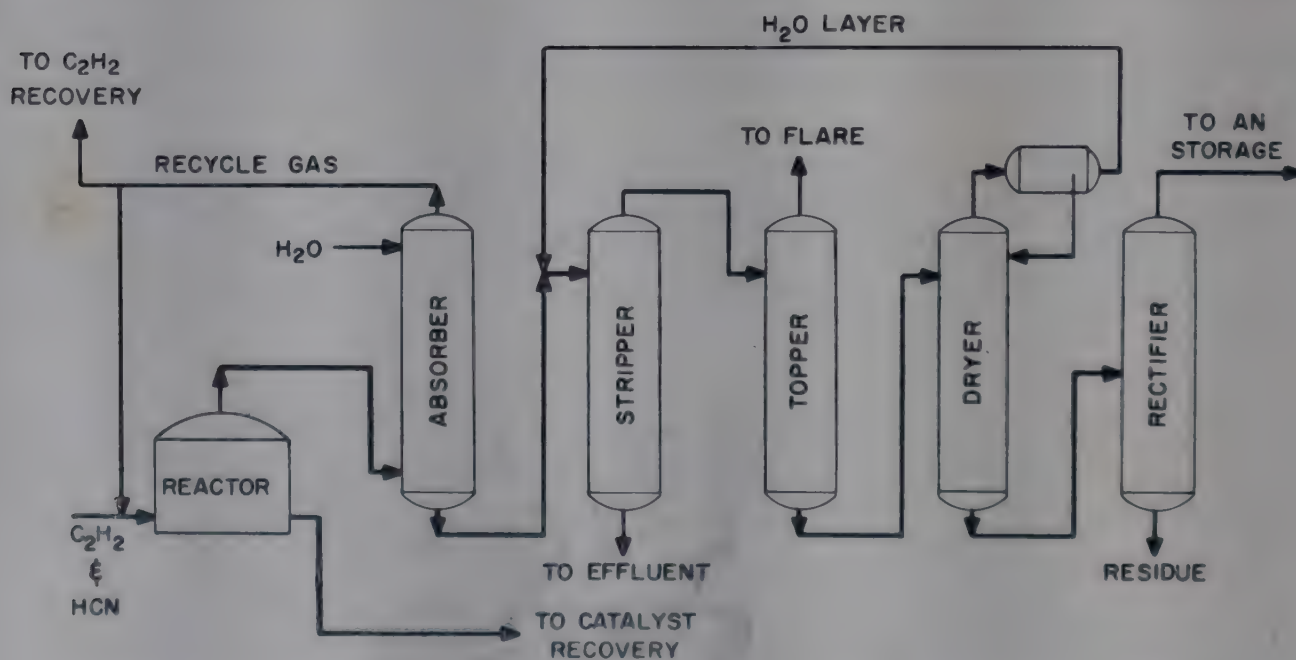


Fig. 1. Liquid phase, acetylene-based process for manufacturing acrylonitrile.

Ludwigshafen and Leverkusen to provide acrylonitrile for Buna-N rubber needed by Germany during World War II (18). The catalyst used was an acidified aqueous solution of cuprous chloride containing 26% copper. Approximately a molar equivalent of ammonium chloride was added to solubilize the cuprous chloride. The process used by American Cyanamid Company at its plant near New Orleans, which is similar to the original German process, was described at the World Petroleum Congress in 1955 (19). A simplified schematic flowsheet, as given at that time, is shown in Figure 1. An excellent generalized process description has also been published (20).

Acetylene and hydrogen cyanide (mole ratio 6:1 to 10:1), are fed into the aqueous cuprous chloride catalyst solution which is maintained at 80–90°C. The effluent from the reactor is cooled and then passed into a water absorber column. The acrylonitrile is thus obtained as a 1–3% solution in water. Excess acetylene and higher acetylenes which are formed in the process leave the top of the scrubber column. The recovered acetylene is purified and recycled.

The solution obtained in the scrubber contains, in addition to acrylonitrile and hydrogen cyanide, several by-products including acetaldehyde, vinylacetylene, methyl vinyl ketone, and 1-cyanobutadiene. This solution is fed to a stripper column where acrylonitrile and low-boiling impurities are separated from the water. The distillate contains about 80% acrylonitrile. It is then fed to a light ends or topper column where relatively volatile impurities are removed, then to a dryer where water is removed by azeotropic distillation; the water layer is returned to the scrubber column. The bottom product from the dryer column is fed to a purification column where acrylonitrile is fractionated from the higher boiling products. Acrylonitrile is recovered from the residue and returned to the purification system while the high-boiling residue, containing a variety of products, including lactonitrile and 1-cyanobutadiene, is sent to waste disposal. Yields in this process are 75–80% based on acetylene and 85–90% based on hydrogen cyanide.

A major problem in the liquid phase process is loss of catalyst activity because of buildup of ammonium chloride and tars during operation. Procedures have been developed for removal, recovery, and replacement of catalyst to maintain constant catalyst activity. Another problem is the variety of other products formed in the process. A product of very high purity is required in many applications and sales specifications are set to meet this requirement. To obtain a product of such purity demands careful control of both reactor operation and product purification.

Much attention has been given to the development of anhydrous catalyst systems for this reaction since water contributes both to side-product formation through hydration reactions and to losses in catalyst activity by hydrolysis reactions. Several solvents are reported in the patent literature, including dimethylformamide (21), pyrrolidone (21), and adiponitrile (22). There are no known commercial liquid phase processes which use an anhydrous catalyst.

Vapor Phase Catalysis. Acrylonitrile can be produced by the vapor phase reaction of acetylene with hydrogen cyanide at temperatures of 400–600°C over a suitable catalyst (23). The catalysts are generally alkali and alkaline earth metal compounds (hydroxide, carbonate, cyanide) on a suitable support (usually charcoal) and may be either in fixed (24) or fluidized beds (25). Deoxygenation of charcoal used in the preparation of the catalyst appears to be important in improving catalyst life and activity (26). Since diluents are desirable in the process, the use of crude acetylene from the Wulff or Sachsse process appears to be feasible (27). A recent patent

suggests the use of a vanadium oxide promoter to improve conversion and reduce the formation of side products (28). Although improved catalyst life is claimed in several patents, published data on catalyst life are not available. Yields of acrylonitrile of up to 98% on acetylene are reported in various patents. The principal by-products in the process are acetonitrile and propionitrile.

There is no published information to indicate that a vapor phase, acetylene-hydrogen cyanide process is in actual commercial operation.

FROM PROPYLENE AND AMMONIA

The catalytic air oxidation of a mixture of propylene and ammonia to produce acrylonitrile was first reported in 1949 (29). The conversion to acrylonitrile was low (6%) but two groups of workers, at Standard Oil Company of Ohio and at Distillers Company, Limited, have independently improved significantly the yields and conversions by the inclusion of steam in the feed mixture and by the use of catalysts containing molybdenum oxide.



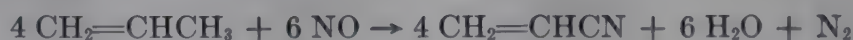
The propylene-ammonia route is used in the Sohio plant which began production in mid-1960. The plant utilizes a fluidized bed reactor operating at moderate temperature (<500°C) and pressure (2–3 atm). The catalyst is probably a bismuth phosphomolybdate on silica gel which has been reported to give a conversion of 33% to acrylonitrile based on propylene (30). Similar catalysts based on molybdenum oxide have been developed by Distillers Company, Limited (31). Other companies that have patents for this process are Ruhr-Chemie, Bayer, Knapsack, and Asahi Kasei (32). It has been claimed that the capital cost of this process is little more than a third of the acetylene process (15).

Major recoverable by-products in the process include hydrogen cyanide and acetonitrile; the yield of acetonitrile amounts to 10–15% of the acrylonitrile produced.

OTHER METHODS

A number of other methods for the preparation of acrylonitrile have been described in the patent literature. Only two of these, the reaction of propylene with nitric oxide and the dehydration of lactonitrile, seem to be of possible commercial use.

Propylene-Nitric Oxide. The reaction of propylene with nitric oxide over a silver oxide on silica catalyst at temperatures of 430–475°C has been reported to give a 12% conversion of propylene to acrylonitrile (33). An improved version of this process may be the basis for Du Pont's plant which is under construction (1961) at Beaumont, Texas (15).



Dehydration of Lactonitrile. The dehydration of lactonitrile has been considered seriously as a route to acrylonitrile; a 30-ton-per-month pilot plant has been operated by Knapsack-Griesheim A.G., Knapsack, Germany. No plans are known for its commercialization, however, possibly because of its complexity as compared to some of the newer processes—notably, the propylene-ammonia oxidation (34,35).

Lactonitrile for this process is prepared by the reaction of acetaldehyde with hydrogen cyanide. The hydrogen cyanide is introduced into a reactor equipped for efficient cooling and good agitation. The pH is then brought to 7.0–7.5 with aqueous

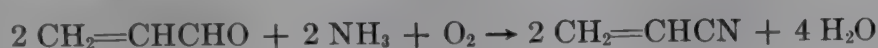
caustic soda and an equivalent amount of acetaldehyde is added with cooling and agitation. After completion of the reaction the product is stabilized by the addition of 0.2 to 0.5% of phosphoric acid. This product, which is 97 to 98% pure, is satisfactory for dehydration to acrylonitrile.



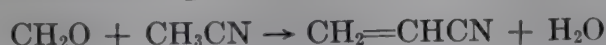
It is known that lactonitrile decomposes rapidly to acetaldehyde and hydrogen cyanide on heating. The key to its successful conversion to acrylonitrile was the development of a technique for rapid heating to the dehydration temperature. In essence, the process first developed consisted of the introduction of a finely divided spray of a mixture of lactonitrile and 85% phosphoric acid into a vacuum furnace held at 600°C. The products leaving the reactor were cooled by injection of water downstream. An alternative method, used in the pilot plant, avoided the use of a vacuum reactor. The lactonitrile (2 parts) and phosphoric acid (1 part) were injected into a stream of combustion gases at 1150°C. The main body of the reactor was kept at 600–620°C; contact time was 3.1 seconds. Upon leaving the reactor the gases were cooled by direct injection of water into the gas stream. Fractional distillation gave acrylonitrile equivalent to 70% of the lactonitrile fed; 23% of the lactonitrile was recovered as acetaldehyde and hydrogen cyanide. These products can be reconverted to lactonitrile and the phosphoric acid concentrated for reuse. Overall acrylonitrile yield in the process was 90–92%.

In addition several other methods of manufacture are of particular interest. These methods, which follow, seem less likely to be of commercial significance.

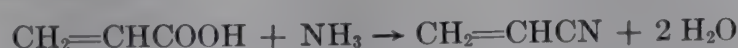
Acrolein, ammonia, and air (36):



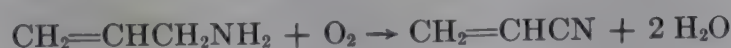
Acetonitrile and formaldehyde (37):



Acrylic acid and ammonia (38):



Dehydrogenation of allylamine by reaction with oxygen (39):



Ethylene and hydrogen cyanide (40):



Economic Aspects

Manufacture of acrylonitrile began in the United States in 1940. In 1950 there was one producer with an annual capacity of 35 million pounds. With the development of acrylic fibers in the 1950s, usage increased to more than 200 million pounds, and present estimated capacity is 400 million pounds. Capacity for another 50 million pounds is under construction. Present producers and their estimated capacities are given in Table 1.

Estimated production, capacity, and prices since 1950 are given in Table 2. The present price (1962), 14.5¢ per pound, is approximately one-third of the 1950–1953 price.

Table 1. United States Production Capacity of Acrylonitrile, 1961

Company	Process	Estimated 1961 capacity, million lb/yr
American Cyanamid	acetylene-hydrogen cyanide	100
Monsanto	acetylene-hydrogen cyanide	100
B. F. Goodrich	acetylene-hydrogen cyanide	35
Du Pont	acetylene-hydrogen cyanide	50
Union Carbide	ethylene cyanohydrin	70
Standard Oil (Ohio)	propylene-ammonia-air	45

Table 2. Estimated Capacity, Production, and Prices of Acrylonitrile, 1954-1960^a

Year	Capacity, million lb/yr	Production, million lb/yr	Price, cents/lb
1954	135	65	31
1955	135	105	31
1956	185	140	27
1957	190	174	26
1958	240	180	26
1959	275	232	26
1960	295	229 (estd)	23
1961	395		14.5

^a Capacity figures from reference 20. Production and prices from U.S. Tariff Commission Reports, "Synthetic Organic Chemicals."

Considerable increases in acrylonitrile production capacity are reported to be planned in Europe and in Japan.

Specifications; Analysis; Toxicity

Commercial acrylonitrile is a high-grade chemical; impurities are present only to the extent of a few parts per million. A few tenths percent of water and a few parts per million of a polymerization inhibitor are added to stabilize the product. Typical sales specifications are given in Table 3.

Analytical Methods. Methods for the analysis for acrylonitrile in high concentrations, dilute aqueous solution, aqueous industrial streams, in air, and in polymer systems have been published. Sources for these may be found in reference 2. In addition, details on analytical methods are readily available from the manufacturer.

A standard method for the analysis of liquid acrylonitrile is the cyanoethylation of *n*-dodecylmercaptan. The excess mercaptan is then back-titrated with standard bromate-iodide reagent in acid solution.

Toxicity. Although acrylonitrile is a highly toxic material, industrial experience with it has been uniformly good. No case of serious poisoning through occupational exposure has come to the author's attention. This remarkable record is due to the care with which it has been handled industrially.

It is toxic by ingestion, inhalation, and contact with the skin. The American Conference of Governmental Industrial Hygienists has established a level of 20 ppm as the maximum allowable in the atmosphere for an exposure of eight hours. This hazard, together with normal hazards in handling low-boiling organic compounds,

Table 3. Typical Sales Specifications for Acrylonitrile^a

Characteristic	Minimum	Maximum
appearance	clear liquid, free from suspended matter	
color (APHA scale)		10
distillation range (at 760 mm), °C		
first drop	74.5	
97%		78.5
refractive index, n_D^{25}	1.3882	1.3892
water, % by weight	0.25	0.45
aldehydes as acetaldehyde, ppm		100
hydrogen cyanide, ppm		5
nonvolatile matter, ppm		100
titration value (basicity), ml 0.1 <i>N</i> HCl		
to lower the pH of 50 ml of acrylonitrile as a 5% aqueous solution to pH 5.0	1	3
total soluble iron as Fe, ppm		0.1
stability, oxygen bomb test, hours	4	
divinylacetylene, ppm		5
methyl vinyl ketone, ppm		300
peroxides as H ₂ O ₂ , ppm		0.5

^a Acrylonitrile is shipped in steel drums and tank cars.

requires that processes be operated in closed systems. Symptoms similar to those of hydrogen cyanide poisoning have been observed in experimental animals. However, the onset and development of symptoms is much slower than with HCN. Acrylonitrile is also a low-grade primary skin irritant. With reasonable precautions, the handling of acrylonitrile should present no major problem either in the plant or in the laboratory (44).

Uses

Three major areas are responsible for about 95% of the present acrylonitrile usage. These are acrylic and modacrylic fibers (qv), nitrile rubber (see Elastomers, synthetic), and plastics (see Styrene and styrene polymers). Several other uses are of considerable importance and it is anticipated that some of them will prove to be of major importance.

In the first few years of its production, acrylonitrile was used in only one major group of products, nitrile rubbers. The rapid growth in the 1950s was due almost entirely to acrylic fibers. Usage in fibers alone amounted to about 150 million pounds in 1960. The excellent properties of the acrylic fibers suggest that they will continue to penetrate the traditional markets for wool but at a lower rate of growth, perhaps, than in the past few years.

In addition to the acrylic fibers, cyanoethylated natural fibers could develop into products of major importance. For example, cyanoethylated cotton (3–4% nitrogen) exhibits marked improvement over the untreated fiber in heat and rot resistance. Dyeing characteristics are modified but appearance and tensile strength are essentially unchanged. Cyanoethylated cotton fabrics are not commercially available (1961) but potential markets are large (41). The cyanoethylation reaction can be applied to other celluloses and polysaccharides. One development is General Electric's current

use of cyanoethylated kraft paper, because of its improved heat resistance and electrical properties, as insulation in heavy-duty transformers. American Cyanamid's Cyano-cel chemically modified cellulose is a thermoplastic with a high dielectric constant. One application is in the fabrication of electroluminescent lamps. (See Cyanoethylation; Cotton.)

Nitrile rubber has many properties which have been important in its development. These include resistance to chemicals, oils, solvents, heat, ageing and abrasion, good dielectric properties, and low-temperature flexibility. Its applications include oil-resistant gaskets, hoses, machinery mountings, tank linings, adhesives, conveyors, nonwoven fabrics, protective clothing, nonmarking shoe heels, and electrical insulation. Estimated acrylonitrile consumption for nitrile rubber application in 1960 was about 30 million pounds.

Acrylonitrile-containing plastics, particularly the acrylonitrile-styrene and acrylonitrile-butadiene-styrene (ABS) polymers, have developed at a good rate in the past few years. Plastics applications accounted for about 25 million pounds of acrylonitrile in 1960 (20). The future market potential for ABS polymer appears to be very bright because of its penetration of the refrigerator and automotive plastics markets. Usage of ABS polymer in 1960 was estimated at 42 million pounds. Published predictions indicate that, by 1965, this market may amount to 150 million pounds (42), thus accounting for about 45-50 million pounds of acrylonitrile. Estimates for 1970 production of these resins range from 300-500 million pounds. Production of acrylonitrile-styrene copolymer in 1960 was about 20 million pounds (43), equivalent to 6 million pounds of acrylonitrile. Although some growth in these polymers is anticipated, it is not expected to be as dramatic as in the ABS polymers.

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ACTINIDES

The actinide elements are a group of chemically similar elements with atomic numbers 89 through 103 (or, more strictly speaking, atomic numbers 90 through 103), and their names, symbols, and atomic numbers are given in Table 1, which also includes information on their discovery. (See also Radioactive elements, natural; Thorium; Uranium; Plutonium; Nuclear reactors; Radioisotopes.)

There is frequently a need for values to be assigned for the atomic weights of the actinide elements. In most cases, each of the elements has a number of isotopes, some of which can be obtained in isotopically pure form. Any precise experimental work would require a value for the isotope or isotopic mixture being used, but where there is a purely formal demand for atomic weights, mass numbers which are chosen on the basis of half-life and availability have customarily been used. A list of these is provided in Table 1.

Thorium and uranium have long been known, and uses dependent on their physical or chemical and not on their nuclear properties were developed prior to the discovery of nuclear fission. The discoveries of actinium and protactinium were among the results of the early studies of naturally radioactive substances. The first trans-

Table 1. The Actinide Elements

Atomic number	Element	Symbol	Atomic weight ^a	Discoverers and date of discovery
89	actinium	Ac	227	A. Debierne, 1899
90	thorium	Th	232	Berzelius, 1828
91	protactinium	Pa	231	O. Hahn and L. Meitner, 1917, and F. Soddy and J. A. Cranston, 1917
92	uranium	U	238	M. H. Klaproth, 1789
93	neptunium	Np	237	E. M. McMillan and P. H. Abelson, 1940
94	plutonium	Pu	242	G. T. Seaborg, E. M. McMillan, J. W. Kennedy, and A. C. Wahl, 1940-41
95	americium	Am	243	G. T. Seaborg, R. A. James, L. O. Morgan, and A. Ghiorso, 1944-45
96	curium	Cm	248	G. T. Seaborg, R. A. James, and A. Ghiorso, 1944
97	berkelium	Bk	249	S. G. Thompson, A. Ghiorso, and G. T. Seaborg, 1949
98	californium	Cf	249	S. G. Thompson, K. Street, Jr., A. Ghiorso, and G. T. Seaborg, 1950
99	einsteinium	E	254	A. Ghiorso, S. G. Thompson, G. H. Higgins, G. T. Seaborg, M. H. Studier, P. R. Fields, S. M. Fried, H. Diamond, J. F. Mech, G. L. Pyle, J. R. Huizenga, A. Hirsch, W. M. Manning, C. I. Browne, H. L. Smith, and R. W. Spence, 1952
100	fermium	Fm	253	A. Ghiorso, S. G. Thompson, G. H. Higgins, G. T. Seaborg, M. H. Studier, P. R. Fields, S. M. Fried, H. Diamond, J. F. Mech, G. L. Pyle, J. R. Huizenga, A. Hirsch, W. M. Manning, C. I. Browne, H. L. Smith, and R. W. Spence, 1953
101	mendelevium	Mv	256	A. Ghiorso, B. G. Harvey, G. R. Choppin, S. G. Thompson, and G. T. Seaborg, 1955
102	—	—	254	A. Ghiorso, T. Sikkeland, J. R. Walton, and G. T. Seaborg, 1958
103	lawrencium	Lw	257	A. Ghiorso, T. Sikkeland, A. E. Larsh, and R. M. Latimer, 1961

^a Mass number of longest lived or more available isotope.

uranium element, neptunium, was discovered during an investigation of nuclear fission, and this event rapidly led to the discovery of the next succeeding element, plutonium. The realization that plutonium as ²³⁹Pu undergoes fission with slow neutrons and thus could be utilized in a nuclear weapon supplied the impetus for its thorough investigation. This research has provided the background of knowledge and techniques for the production and identification of nine more transuranium elements.

Thorium, uranium, and plutonium are well known for their role as the basic fuels (or sources of fuel) for the release of nuclear energy. The importance of the remainder of the actinide group lies at present for the most part in the realm of pure research.

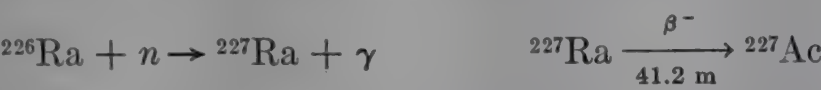
Source

Only the first six members of the actinide group have been found to occur in nature. Actinium and protactinium are decay products of the naturally occurring uranium isotope ²³⁵U, but the concentrations present in uranium minerals are small

and the methods involved in obtaining them from the natural source are very difficult and very tedious in contrast to the relative ease with which the elements can be synthesized. Thorium and uranium occur widely in the earth's crust in combination with other elements, and, in the case of uranium, in significant concentrations in the oceans. The extraction of these two elements from their ores has been studied intensively and forms the basis of an extensive technology. Neptunium and plutonium are present in trace amounts in nature, being formed by neutron capture in uranium ores, but obtaining these elements from this source is not feasible because the concentrations involved are exceedingly small. Thus, with the exceptions of uranium and thorium, all of the actinide elements are synthetic in origin for practical purposes, ie, they are products of nuclear reactions wherein one element is converted into another by means of irradiations with neutrons or bombardments with protons, helium ions, deuterons, or ions heavier than helium ions ("heavy ions"). High neutron fluxes are available in modern nuclear reactors, and the most feasible method for preparing actinium, protactinium, and most of the transuranium elements is through the neutron irradiation of elements of high atomic number.

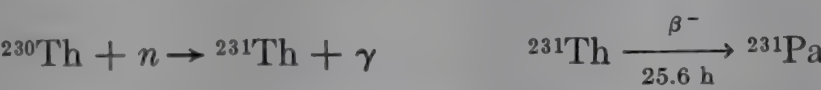
The synthesis of these elements will be discussed in order of increasing atomic number.

Actinium can be prepared by the transmutation of radium,



and milligram amounts have been obtained in this way. The actinium is isolated by means of solvent extraction or ion exchange.

Protactinium can be produced in the nuclear reactions,

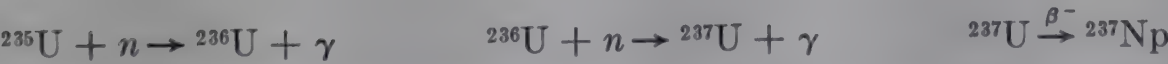


The methods for the recovery of protactinium include coprecipitation, solvent extraction, ion exchange, and volatility procedures. All of these, however, are rendered difficult by the extreme tendency of protactinium(V) to form polymeric ionic species and then colloidal particles. These are not extractable from water by organic solvents; losses may occur by adsorption to containers; and protactinium may be adsorbed and carried on any precipitate present.

Considerable amounts of neptunium (^{237}Np) are formed as a by-product of the large-scale synthesis of plutonium in nuclear reactors which utilize ^{235}U and ^{238}U as fuel. The following transmutations occur:

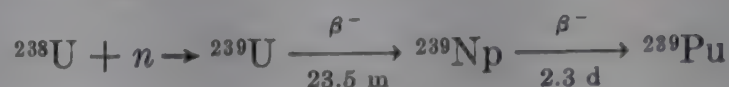


and



The wastes from uranium and plutonium processing of the reactor fuel usually contain the neptunium. Precipitation, solvent extraction, ion exchange, and volatility procedures can be used to isolate and purify the neptunium.

Plutonium as the important isotope ^{239}Pu is prepared in multikilogram amounts in nuclear reactors. It is produced by the following reactions, wherein the excess neutrons produced by the fission of ^{235}U are captured in ^{238}U to yield ^{239}Pu .



A variety of industrial-scale processes have been devised for the recovery and purification of plutonium. These can be divided, in general, into the categories of precipitation, solvent extraction, and ion exchange.

The isotope ^{238}Pu , produced by the reactions



is an important fuel for isotopically powered energy sources used for terrestrial and space satellite applications.

Quantities of americium as ^{241}Am can be obtained by the processing of reactor-produced plutonium. Much of this material contains an appreciable proportion of ^{241}Pu , which is the parent of ^{241}Am . Separation of the americium is effected by precipitation, ion exchange, or solvent extraction.

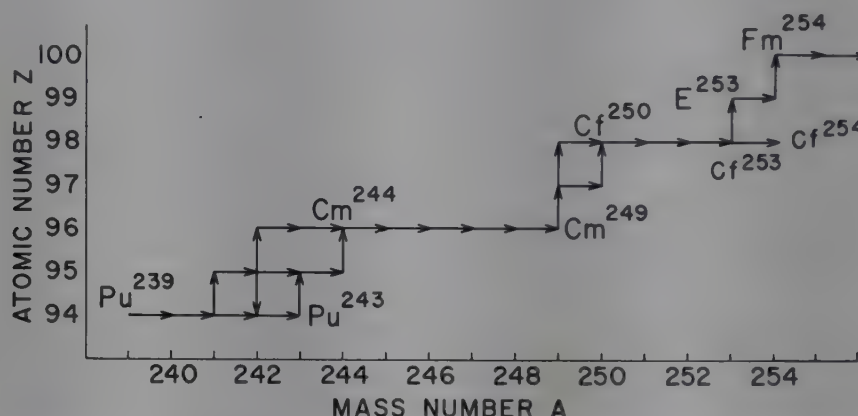


Fig. 1. Nuclear reactions for the production of heavy elements by intense slow neutron irradiation.

The nuclear reaction sequences of neutron captures and beta decays involved in the preparation of the elements with atomic numbers 95 through 100 by means of the slow neutron irradiation of ^{239}Pu are indicated in Figure 1. The irradiations are performed by placing the parent material in the core of a high-neutron flux reactor where fluxes of neutrons in excess of 10^{14} neutrons per square centimeter per second may be available. Figure 2 gives an indication of the time required for the preparation of various heavy isotopes from ^{239}Pu as the starting material. For example, beginning with one kilogram of ^{239}Pu , about one milligram of ^{252}Cf would be present after five to ten years of continuous irradiation (not possible in practice) at a neutron flux of 3×10^{14} neutrons per square centimeter per second. The Materials Testing Reactor at the National Reactor Testing Station at Arco, Idaho, has been the source of gram quantities of curium isotopes and multimicrogram quantities of californium and berkelium. Much larger quantities can be produced by irradiating larger quantities of plutonium in production reactors, followed by irradiation of the curium thus produced in higher neutron flux reactors.

Ion exchange (qv; see also Chromatography) is the most important procedure for the separation and chemical identification of curium and higher elements. This technique is selective and rapid and has been the key to the discovery of the transcurium elements in that the elution order and approximate peak positions for the undiscovered

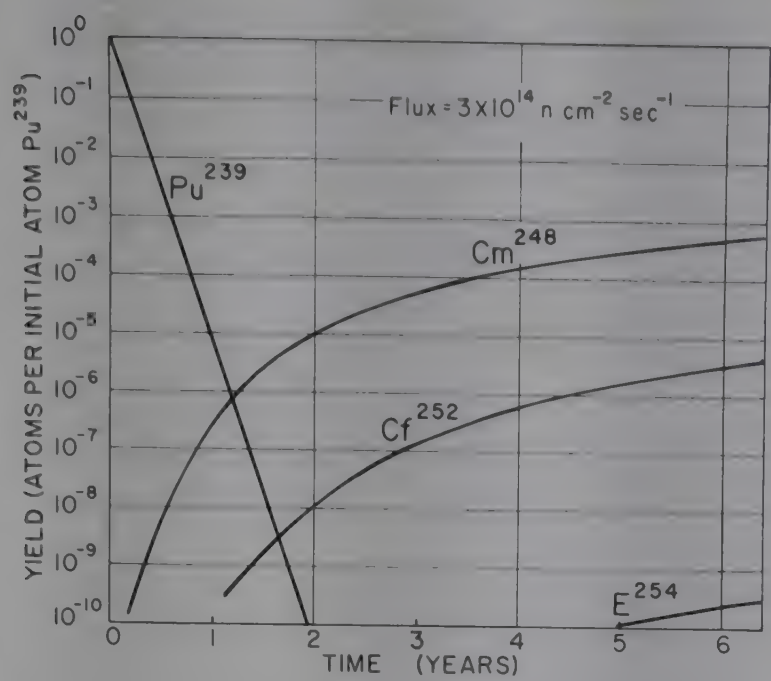


Fig. 2. Production of heavy nuclides by the irradiation of ^{239}Pu at a flux of 3×10^{14} neutrons per square centimeter per second.

elements were predicted with considerable confidence. Thus, the first experimental observation of the chemical behavior of a new element is apt to be its ion exchange behavior—an observation coincident with its identification. Further exploration of the chemistry of the element may be subject to considerable delay, pending the production of larger amounts.

There are many similarities in the chemical properties of the lanthanide elements (see Rare earth metals) and those of the actinide elements, especially where the elements are compared in the same state of oxidation.

A striking example of this resemblance is furnished by their ion exchange behavior. Figure 3 shows the comparative elution data for tripositive actinide and lanthanide ions obtained by the use of the ion exchange resin Dowex-50 (a copolymer of styrene and divinylbenzene with nuclear sulfonic acid groups) and the eluting agent ammonium α -hydroxyisobutyrate. It can be seen that in this system the elutions occur in the inverse order of atomic number. The elution sequence depends on a balance between the adherence to the resin and the stability of the complex ion formed with the eluting agent and may be correlated with the variation of ionic radius with atomic number.

Actinide ions of the III, IV, V, and VI oxidation states can be adsorbed by cation exchange resins and, in general, can be desorbed by elution with, for example, the anions chloride, nitrate, citrate, lactate, α -hydroxyisobutyrate, and ethylenediamine-tetraacetate.

Ion exchange separations can also be made by the use of a polymer with exchangeable anions; in this case, the lanthanide or actinide elements must be initially present as complex ions. The ion exchange resins Dowex-1 (a copolymer of styrene and divinylbenzene with quaternary ammonium groups) and Amberlite IRA-400 (a quaternary ammonium polystyrene) have been used successfully. The order of elution is often the reverse of that from cationic exchange resins.

It is possible to prepare very heavy elements in thermonuclear explosions, owing to the very intense, although brief (order of a microsecond), neutron flux furnished by the explosion. Einsteinium and fermium were first produced in this way; they were

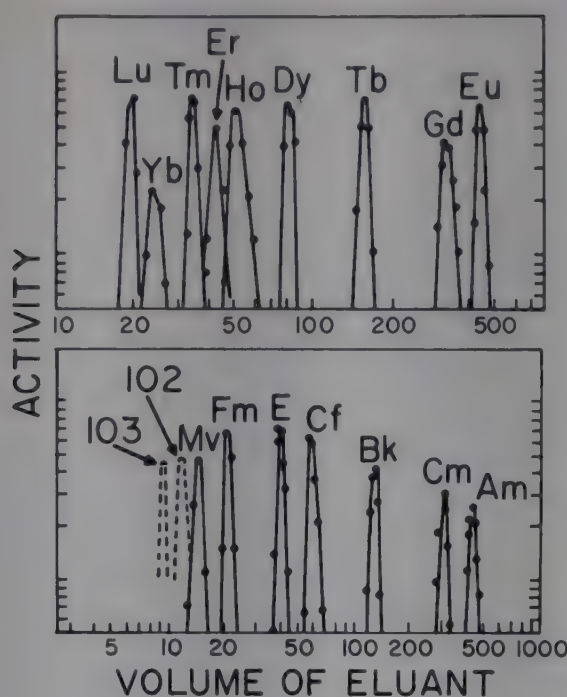


Fig. 3. The elution of tripositive actinide and lanthanide ions. Dowex-50 ion exchange resin was used with ammonium α -hydroxyisobutyrate as the eluant. The positions predicted for the short-lived elements 102 and 103 are indicated by broken lines.

discovered in the fallout materials from the first thermonuclear explosion (the "Mike" shot) staged in the Pacific in November of 1952. It is possible that elements with atomic numbers greater than 100 would have been found had the debris been examined very soon after the explosion. The preparative process involved is multiple neutron capture in the uranium in the device, which is followed by a sequence of beta decays. For example, the synthesis of ^{255}Fm in the Mike explosion was via the production of ^{255}U from ^{238}U , followed by a long chain of short-lived beta decays,



all of which occur after the neutron capture reactions are completed.

The process of neutron irradiation in high-flux reactors cannot be used to prepare the elements beyond fermium (except at extremely high neutron fluxes) because some of the intermediate isotopes which must capture neutrons have half-lives so short as to preclude their presence in the appreciable concentrations that are necessary. The transfermium elements have been prepared in charged-particle bombardments, but in such syntheses the limited availability of target materials of high atomic number, the small reaction yields, and the difficulties intrinsic in the isolation of very short-lived substances present very serious problems. Nonchemical separations of short-lived isotopes from the target materials have been carried out during bombardments, and these will be described in the following paragraphs.

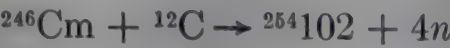
Two isotopes of mendelevium have been produced by the helium-ion bombardment of einsteinium isotopes,



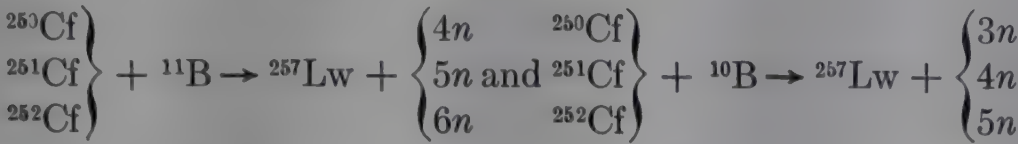
In both preparations, the mendelevium isotopes were isolated from the target material by collecting on a gold foil the atoms of mendelevium which recoiled owing to the momentum of the beam of helium ions. In the experiments wherein mendelevium was first prepared (as ^{256}Mv) only a few atoms of the element were produced, but these were successfully separated chemically and were characterized as having the atomic number

101. A fairly elaborate adaptation of this recoil method has been used in the discoveries of elements 102 and 103.

Elements 102 and 103 (lawrencium) are prepared by heavy-ion bombardments. For element 102, the discovery reaction is



and, for element 103 (obtained by bombarding a target consisting of a mixture of californium isotopes with ¹⁰B and ¹¹B ions),



Element 102 (²⁵⁴102 half-life, 3 s) and lawrencium (²⁵⁷Lw half-life, 8 s) were separated from the target material by a nonchemical technique, which involves the electrostatic collection of the product atoms that recoil from the target and that retain a positive charge when stopped in helium gas. Identification of these elements is based on decay

Table 2. Actinide Nuclides Suitable for Investigations with Weighable Quantities

Element	Isotope	Half-life
actinium	²²⁷ Ac	22.0 y
thorium	²³² Th	1.39 × 10 ¹⁰ y
protactinium	²³¹ Pa	3.43 × 10 ⁴ y
uranium	²³⁸ U ^a	4.50 × 10 ⁹ y
neptunium	²³⁶ Np	>5000 y
	²³⁷ Np	2.20 × 10 ⁶ y
plutonium	²³⁹ Pu	86.4 y
	²³⁹ Pu	24,360 y
	²⁴⁰ Pu	6580 y
	²⁴¹ Pu	13.0 y
	²⁴² Pu	3.73 × 10 ⁵ y
	²⁴⁴ Pu	7.6 × 10 ⁷ y
americium	²⁴¹ Am	458 y
	²⁴² Am	~100 y
	²⁴³ Am	7950 y
curium	²⁴² Cm	162.5 d
	²⁴³ Cm	35 y
	²⁴⁴ Cm	19 y
	²⁴⁵ Cm	1.4 × 10 ⁴ y
	²⁴⁶ Cm	5000 y
	²⁴⁷ Cm	≥ 4 × 10 ⁷ y
	²⁴⁸ Cm	4.7 × 10 ⁵ y
	²⁵⁰ Cm	2 × 10 ⁴ y
berkelium	²⁴⁷ Bk	7 × 10 ³ y
	²⁴⁹ Bk	270 d
californium	²⁴⁹ Cf	400 y
	²⁵⁰ Cf	9.3 y
	²⁵¹ Cf	660 y
	²⁵² Cf	2.2 y
einsteinium	²⁵³ E	20 d
	²⁵⁴ E	280 d

^a Natural mixture (²³⁸U—99.3%, ²³⁵U—0.72%, and ²³⁴U—0.006%). Half-life given is for the major constituent ²³⁸U.

characteristics or the genetic correlation with daughter activities of previously established atomic number. The method has general application to experimental work involving the separation of other nuclides of transient existence.

Cyclotrons of the conventional type can be used to accelerate heavy ions; in addition, linear accelerators designed for this express purpose are in operation in several laboratories throughout the world. The Heavy Ion Linear Accelerator (Hilac) at the University of California in Berkeley, in which elements 102 and 103 were first synthesized, is an example of such a machine.

Isotopes sufficiently long-lived for work in weighable amounts are obtainable, at least in principle, for all of the actinide elements through einsteinium (99), and these isotopes with their half-lives are listed in Table 2. It appears that it will always be necessary to study the elements fermium and above by means of the tracer technique (except for some very special experiments) because only isotopes with short half-lives are known.

Experimental Methods of Investigation

All of the actinide elements are radioactive, and special equipment and shielded facilities are generally necessary for their manipulation. On a laboratory scale, enclosed containers (gloved boxes) are used to prevent the spread of radioactive substances. In some work, all operations are performed by remote control. Neptunium in the form of the isotope ^{237}Np is relatively safe to work with in chemical investigations. Because of the existence of very large quantities of the fissionable isotope ^{239}Pu , the physiological toxicity of plutonium deserves emphasis. In this form plutonium is one of the most dangerous known poisons by reason of its intense alpha radioactivity (1.4×10^8 alpha particles per minute per milligram) and of its physiological behavior. Ingested plutonium may be transferred to the bone and over a period of time give rise to neoplasms.

The study of the chemical behavior of concentrated preparations of short-lived isotopes is complicated by the rapid production of hydrogen peroxide in aqueous solutions and the destruction of crystal lattices in solid compounds. These effects are brought about by high-energy alpha particles released in the decay process.

Most chemical investigations with plutonium to date have been performed with ^{239}Pu , but the isotopes ^{242}Pu and ^{244}Pu are more suitable for such work because of their longer half-lives and consequently lower specific activities. Work on the chemical properties of americium has been carried out with ^{241}Am , which is also difficult to handle since it has a relatively high specific alpha radioactivity, emitting about 7×10^9 alpha particles per minute per milligram. The isotope ^{243}Am has a specific alpha activity about twenty times less than ^{241}Am and is thus a more attractive isotope for chemical investigation. Curium has been investigated on a macroscopic scale, whereby the isotopes principally used were ^{242}Cm (having a specific disintegration rate of approximately 10^{14} alpha particles per minute per milligram) and ^{244}Cm (with a specific disintegration rate of approximately 2×10^{12} alpha particles per minute per milligram). Such work with ^{242}Cm is extremely difficult, and use of this isotope was discontinued after some of the earliest work with it. For example, the heat produced by radioactivity would evaporate a millimolar solution of ^{242}Cm to dryness in a short time. Determination of compound structures by x-ray analysis is almost impossible when ^{242}Cm is used, because of the very rapid damage to crystal lattices noted above, and somewhat difficult when ^{244}Cm is employed. The heavier curium isotopes are

less radioactive and offer great advantage in experimental work. Of the curium isotopes, ^{248}Cm appears to be potentially the most useful for chemical studies. Berkelium (as ^{249}Bk) and californium (as a mixture of the isotopes ^{249}Cf , ^{250}Cf , ^{251}Cf , and ^{252}Cf) were isolated in weighable amounts in 1958, and their macroscopic properties have been studied in this manner since that date. These elements were synthesized in the long-term neutron irradiation of lighter nuclides. Einsteinium, as the isotope ^{253}E (half-life, 20 d) was isolated in macroscopic quantity for the first time in 1961 by B. B. Cunningham, J. C. Wallmann, L. Phillips, and R. C. Gatti. The isotope ^{254}E (half-life, 280 d) is more useful for work with macroscopic quantities. Weighable amounts of berkelium, californium, and einsteinium are very difficult to handle because of their intense radioactivity. Spontaneous fission is a mode of decay for ^{252}Cf (half-life, 2.2 y), one microgram of which emits approximately 2×10^8 neutrons per minute, and the chief mode of decay of ^{254}Cf (half-life, 56 d), one microgram of which emits approximately 8×10^{10} neutrons per minute. Californium produced in the highest flux reactors unfortunately contains ^{254}Cf , and this makes it very difficult to handle. In work with any more than a few micrograms of ^{252}Cf , or with less than microgram amounts of ^{254}Cf , it is necessary to do all manipulations by remote control, which is exceedingly cumbersome on such a small scale.

Special techniques for experimentation with the actinide elements have been devised because of the potential health hazard to the experimenter and because the amounts of material available are sometimes so very small. In addition, investigations are frequently carried out on the tracer scale, where the substance under examination is present in very low concentration and its radioactivity offers a means for detecting its presence. Such procedures are, of course, applied to work with the heavier transcurium elements, where only a few score atoms may be available; they were used in the earliest work for all the transuranium elements and continue to be used to some extent for these elements. Tracer studies offer a method for obtaining knowledge of oxidation states, formation of complex ions, and the solubility of various compounds. These techniques are, of course, not applicable to some other important fields of investigation, such as crystallography, metallurgy, and spectroscopy.

Microchemical or ultramicrochemical techniques are used extensively in chemical studies of actinide (and other) elements. If extremely small volumes are used, microgram or lesser quantities of material can give relatively high concentrations in solution. Balances of sufficient sensitivity have been developed to permit the taking of quantitative measurements with these minute quantities of material; some balances measure magnetic forces due to the paramagnetic nature of the ions. Since the amounts of material involved are too small to be seen with the unaided eye, the actual chemical work is usually done on the mechanical stage of a microscope, where all of the essential apparatus is in view. Compounds prepared on such a small scale have been successfully identified by x-ray crystallographic methods.

Position in the Periodic Table and Electronic Structure

Prior to 1944, the location of the heaviest elements in the periodic table had been a matter of question, and the elements thorium, protactinium, and uranium were commonly placed immediately below the elements hafnium, tantalum, and tungsten. In 1944, however, on the basis of chemical studies of neptunium and plutonium, the similarity between the actinide and the lanthanide elements was recognized. The intensive

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57-71 La Series	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89-103 Ac Series	(104)	(105)	(106)	(107)	(108)										

Lanthanide Series	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinide Series	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102	103 Lw

Fig. 4. Periodic table of the elements.

study of the heaviest elements has made it certain that a series of elements similar to the lanthanide series begins at actinium. Figure 4 shows the position of the actinide and the lanthanide elements in the periodic table. Corresponding pairs of elements show similarities in certain basic properties, notably (1) resemblances in spectroscopic and magnetic behavior which arise because of the similarity of electronic configurations for the ions of the homologous elements in the same state of oxidation, and (2) correspondences in crystallographic properties, owing to the near matching of ionic radii for ions of the same charge. The two series are not, however, entirely comparable. A difference lies in the oxidation states. The tripositive-state characteristic of lan-

Table 3. Electronic Configurations for Gaseous Atoms of Actinide and Lanthanide Elements

Atomic number	Element	Electronic configuration ^a	Atomic number	Element	Electronic configuration ^b
89	actinium	6d7s ²	57	lanthanum	5d6s ²
90	thorium	6d ² 7s ²	58	cerium	4f5d6s ²
91	protactinium	5f ² 6d7s ²	59	praseodymium	4f ³ 6s ²
92	uranium	5f ³ 6d7s ²	60	neodymium	4f ⁴ 6s ²
93	neptunium	5f ⁴ 6d7s ²	61	promethium	4f ⁵ 6s ²
94	plutonium	5f ⁶ 7s ²	62	samarium	4f ⁶ 6s ²
95	americium	5f ⁷ 7s ²	63	europium	4f ⁷ 6s ²
96	curium	5f ⁷ 6d7s ²	64	gadolinium	4f ⁷ 5d6s ²
97	berkelium	(5f ⁸ 6d7s ² or 5f ⁹ 7s ²)	65	terbium	4f ⁹ 6s ²
98	californium	(5f ¹⁰ 7s ²)	66	dysprosium	4f ¹⁰ 6s ²
99	einsteinium	(5f ¹¹ 7s ²)	67	holmium	4f ¹¹ 6s ²
100	fermium	(5f ¹² 7s ²)	68	erbium	4f ¹² 6s ²
101	mendelevium	(5f ¹³ 7s ²)	69	thulium	4f ¹³ 6s ²
102	—	(5f ¹⁴ 7s ²)	70	ytterbium	4f ¹⁴ 6s ²
103	lawrencium	(5f ¹⁴ 6d7s ²)	71	lutetium	4f ¹⁴ 5d6s ²

^a Beyond radon. The configurations enclosed in parentheses are predicted ones.
^b Beyond xenon.

hanide elements does not appear in aqueous solutions of thorium and protactinium and does not become the most stable oxidation state in aqueous solution until americium is reached. The elements uranium through americium have several oxidation states, and there is no analogous example among the lanthanide elements. These differences can be interpreted as resulting from the proximity in the energy of the 7s, 6d, and 5f electronic levels in this region.

Table 3 presents the electronic configuration or the best prediction for the electronic configuration of the actinide elements. Similar information for the lanthanide elements is given for purposes of comparison. As is indicated, fourteen 4f electrons are added in the lanthanide series beginning with cerium (atomic number 58) and ending with lutetium (atomic number 71); and in the actinide elements, fourteen 5f electrons are added beginning formally with thorium and ending with lawrencium (atomic number 103). In the cases of actinium, thorium, uranium, and americium, the configurations were determined from an analysis of spectroscopic data obtained in connection with the measurement of the emission lines from neutral and charged gaseous atoms. The knowledge of the electronic structures for protactinium, neptunium, plutonium, and curium results from atomic beam experiments.

Measurements of paramagnetic susceptibility, paramagnetic resonance, light absorption, and crystal structure, in addition to a consideration of chemical and other properties, have provided a great deal of information about the electronic configurations of the aqueous actinide ions and of actinide compounds. In general, all of the electrons beyond the radon core in the actinide compounds and in aqueous actinide ions are in the 5f shell. There are exceptions (such as U_2S_3) and subnormal compounds (such as Th_2S_3) where 6d electrons are present.

Properties

The close chemical resemblance between the actinide elements permits their chemistry to be described for the most part in a correlative way.

Oxidation States. The oxidation states of the actinide elements are summarized in Table 4. The most stable states are designated by bold type, and those which are

Table 4. The Oxidation States of the Actinide Elements

Atomic number Element	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 E	100 Fm
Oxidation states	3	(3) 4	(3) 4 5	3 4 5 6	3 4 5 6	3 4 5 6	3 4 5 6	3 4	3 4	3	3	3

very unstable are indicated by parentheses. These latter states do not exist in aqueous solution and have been produced only in solid compounds although protactinium(III) may be an exception. The IV state of curium is limited to CmO_2 (solid) and CmF_4 (solid) and a complex ion stable in highly concentrated lithium fluoride solution.

The actinide elements exhibit uniformity in ionic types. In acidic aqueous solution, there are four types of cations, and these and their colors are listed in Table 5. The open spaces indicate that the corresponding oxidation states do not exist in aqueous solution. The color of plutonium(V) has not been observed, but is deduced from

Table 5. Ion Types and Colors for Actinide Ions

Element	M ³⁺	M ⁴⁺	MO ₂ ⁺	MO ₂ ²⁺
actinium	colorless			
thorium		colorless		
protactinium		colorless	(colorless)	
uranium	red	green	(color unknown)	yellow
neptunium	blue to purple	yellow-green	green	pink to red
plutonium	blue to violet	tan to orange-brown	(reddish purple)	yellow to pink-orange
americium	pink	unknown	yellow	rum-colored
curium	colorless	unknown		

the absorption spectrum of its aqueous solution. Protactinium(V) usually exists in aqueous solution as a highly polymerized colloid, and it seems unlikely that PaO₂⁺ is present in such solutions. The status of protactinium(III) in aqueous solution is not known. The wide variety of colors exhibited by actinide ions is characteristic of a transition series of elements.

Corresponding ionic types are similar in chemical behavior although the oxidation-reduction relationships and, therefore, the relative stabilities differ from element to element. The ions MO₂⁺ and MO₂²⁺ are stable with respect to their binding of oxygen atoms and remain unchanged through a great variety of chemical treatment. They behave as single entities with properties intermediate to singly or doubly charged ions and ions of similar size but of higher charge.

The oxidation potentials for the actinide elements are shown on the following page. These are "formal potentials," defined as the measured potentials corrected to unit concentration of the substances entering into the reactions, on the basis of the hydrogen-hydrogen-ion couple taken as zero volts, and with no corrections made for activity coefficients. The measured potentials were established by cell, equilibrium, and heat of reaction determinations. The potentials for acid solution were generally measured in 1*M* perchloric acid, and, for alkaline solution, in 1*M* sodium hydroxide. Estimated values are given in parentheses.

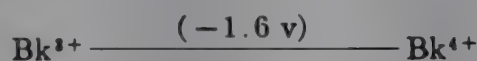
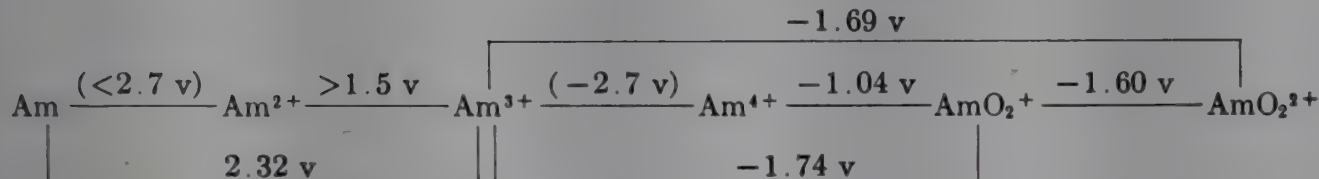
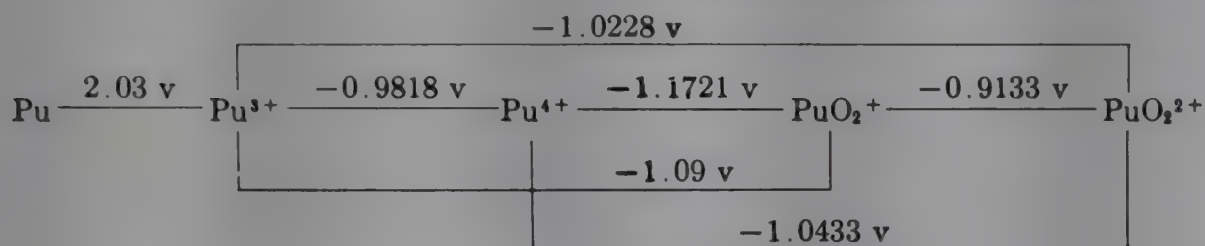
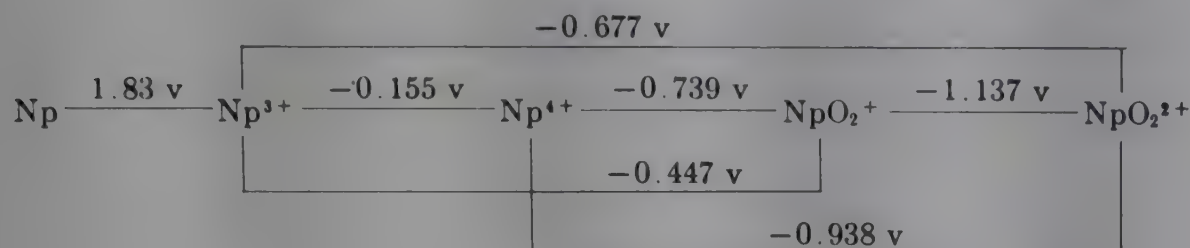
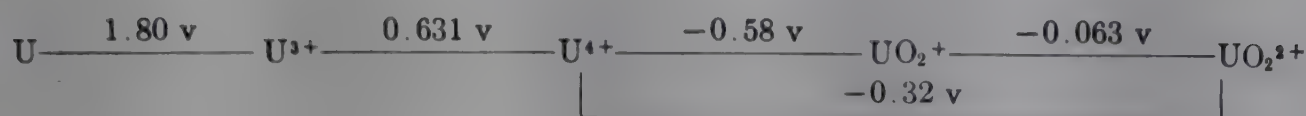
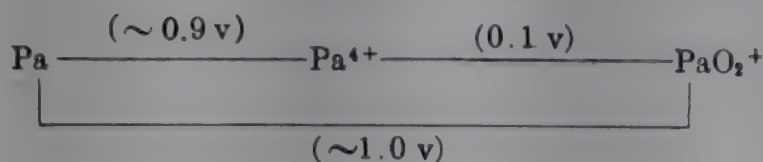
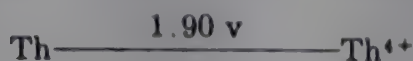
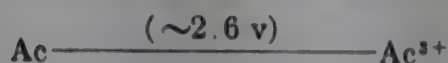
The M³⁺—M⁴⁺ and MO₂⁺—MO₂²⁺ couples are readily reversible and reactions are rapid with other one-electron reducing or oxidizing agents that involve no bond changes. The rate varies with reagents that normally react by two-electron or bond-breaking changes. The M³⁺—MO₂⁺, M³⁺—MO₂²⁺, M⁴⁺—MO₂⁺, and M⁴⁺—MO₂²⁺ couples are not reversible, presumably because of slowness introduced in the making and breaking of oxygen bonds.

Table 6 presents a summary of the oxidation-reduction characteristics of actinide ions. The disproportionation reactions of UO₂⁺, Pu⁴⁺, PuO₂⁺, and AmO₂⁺ are very complicated and have been studied extensively. In the case of plutonium, the situation is especially complex: Four oxidation states of plutonium(III, IV, V, and VI) can exist together in aqueous solution in equilibrium with each other at appreciable concentrations.

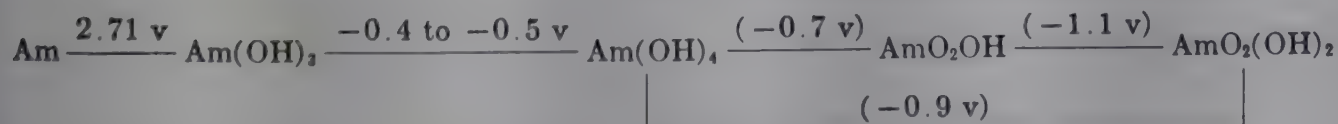
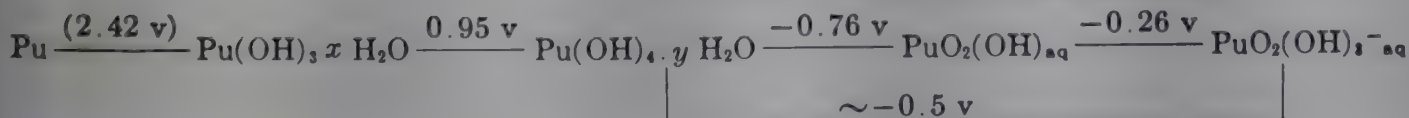
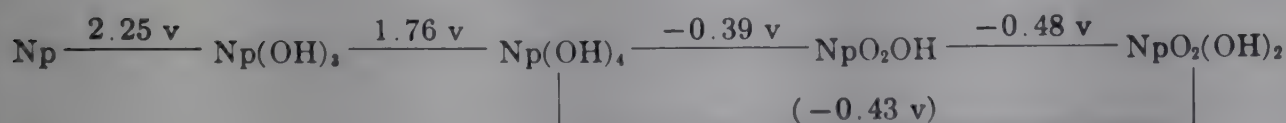
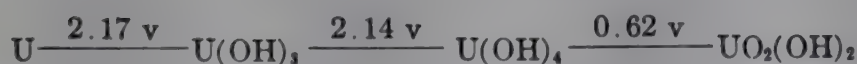
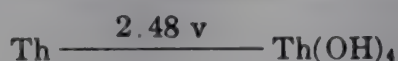
Hydrolysis and Complex Ion Formation. Hydrolysis and complex ion formation are closely related phenomena and will thus be discussed together.

Of the actinide ions, the small, highly charged M⁴⁺ ions exhibit the greatest degree of hydrolysis and complex ion formation. For example, the ion Pu⁴⁺ hydrolyzes extensively and also forms very strong anion complexes. The hydrolysis of Pu⁴⁺ is of especial interest in that polymers which exist as positive colloids can be produced;

Acidic Aqueous Solution



Alkaline Aqueous Solution



their molecular weight and particle size depend on the preparative method. Polymeric plutonium with a molecular weight as high as 10^{10} has been reported.

The degree of hydrolysis or complex ion formation decreases in the order $\text{M}^{4+} > \text{MO}_2^{2+} > \text{M}^{3+} > \text{MO}_2^+$. Presumably the relatively high tendency toward hydrolysis and complex ion formation of MO_2^{2+} ions is related to the high concentration

of charge on the metal atom. On the basis of increasing charge and decreasing ionic size, it could be expected that the degree of hydrolysis for each ionic type would increase with increasing atomic number. For the ions M^{4+} and M^{3+} , beginning at about uranium, such a regularity of hydrolytic behavior is observed, but for the remaining two ions MO_2^+ and MO_2^{2+} the degree of hydrolysis decreases with increasing atomic number, thus indicating the operation of more complicated factors than simple size and charge.

Table 6. Stability of Actinide Ions in Aqueous Solution

Ion	Stability
U^{3+}	aqueous solutions evolve hydrogen on standing
Np^{3+}	stable to water, but readily oxidized by air to Np^{4+}
Pu^{3+}	stable to water and air, but easily oxidized to Pu^{4+} ; oxidizes slightly under the action of its own alpha radiation (in form of ^{239}Pu)
Am^{3+}	stable; difficult to oxidize
Cm^{3+}	stable
Bk^{3+}	stable; can be oxidized to Bk^{4+}
Cf^{3+}	stable
E^{3+}	stable
Fm^{3+}	stable
Mv^{3+}	stable
U^{4+}	stable to water, but slowly oxidized by air to UO_2^{2+}
Np^{4+}	stable to water, but slowly oxidized by air to NpO_2^+
Pu^{4+}	stable in concentrated acid, eg, 6M HNO_3 , but disproportionates to Pu^{3+} and PuO_2^{2+} at lower acidities
Am^{4+}	known in solution only as complex fluoride ion
Cm^{4+}	known in solution only as complex fluoride ion
Bk^{4+}	stable; easily reduced to Bk^{3+}
UO_2^+	disproportionates to U^{4+} and UO_2^{2+} ; most stable at pH 2–4
NpO_2^+	stable; disproportionates only at high acidities
PuO_2^+	always tends to disproportionate to Pu^{4+} and PuO_2^{2+} (ultimate products); most stable at very low acidities
AmO_2^+	disproportionates in strong acid to Am^{3+} and AmO_2^{2+} ; reduces fairly rapidly under the action of its own alpha radiation at low acidities (in form of ^{241}Am)
UO_2^{2+}	stable; difficult to reduce
NpO_2^{2+}	stable; easy to reduce
PuO_2^{2+}	stable; easy to reduce; reduces slowly under the action of its own alpha radiation (in form of ^{239}Pu)
AmO_2^{2+}	reduces fairly rapidly under the action of its own alpha radiation (in form of ^{241}Am)

The extensive hydrolysis of protactinium in its important V oxidation state is noteworthy because it is a trait which makes the chemical investigation of protactinium extremely difficult. Simple ions of protactinium(V) do not exist in aqueous solution, and, to prevent hydrolysis, the ion must be held in solution by a complexing agent as, for example, fluoride ion.

The tendency toward complex ion formation of the actinide ions is determined largely by the factors of ionic size and charge. Although there is some variation within each of the ionic types, the order of complexing power of different anions is, in general, in the order fluoride > nitrate > chloride > perchlorate for mononegative anions and carbonate > oxalate > sulfate for dinegative anions. The actinide ions form somewhat stronger complex ions than homologous lanthanide ions.

Table 7. Properties of Actinide Metals

Element	Melting point, °C	Heat of vaporization and boiling point, kcal/mole	Crystal structure					Density, g/cm³ at °C	
			Phase	Range of stability, °C	Symmetry	Lattice parameters, Å			
						a ₀	b ₀		c ₀
actinium thorium	1100 ± 50	(70)			FC cubic	5.311			
	1750	130-177 (3000-4200°C)	α	RT to 1400	FC cubic	5.086			11.724, 25°
protactinium			β	1400 to 1750	BC cubic	4.11			
	(<1873)				tetragonal	3.925	3.238		15.37
uranium		106.7 (3818°C)	α	RT to 668	orthorhombic	2.8541	5.8692	4.9563	19.04, 25°
	1132		β	668 to 774	tetragonal	10.759		5.656	18.11, 720°
neptunium			γ	774 to 1132	BC cubic	3.525			18.06, 805°
	637 ± 2		α	RT to 280 ± 5	orthorhombic	3.52	4.887	6.663	20.45, 25°
plutonium			β	280 ± 5 to 577 ± 5	tetragonal	4.895		3.387	19.36, 313°
	639.5	80.46 ± 0.34 (3235°C)	(γ	577 ± 5 to 637 ± 2	cubic)	(3.52)			(18.00, 600°)
americium			α	RT to 122	monoclinic	6.1835	4.8244	10.973	19.737, 25°
			β	122 to 203	BC monoclinic				17.77, 150°
			γ	203 to 317	orthorhombic	3.1603	5.7624	10.141	17.19, 210°
			δ	317 to 453	FC cubic	4.6370			15.92, 320°
			δ'	453 to 477	tetragonal	4.701		4.489	15.99, 465°
					c/a = 0.955				
			ε	477 to 640	BC cubic	3.638			16.48, 500°
	995 ± 4°C	57 (2607°C)	α	RT to ~600	hexagonal	3.468		11.240	13.67, 20°

NOTE: Estimates and uncertain quantities in parentheses.

Table 8. Properties and Crystal Structure Data for Some Important Actinide Compounds

Compound	Color	Melting point, °C	Crystal structure					Density, g/cm ³
			Symmetry	Space group or structure type	Lattice parameters, Å			
					a ₀	b ₀	c ₀	
ThH ₂	black		tetragonal		4.10		5.03	9.20
Th ₄ H ₁₆	black		cubic		9.11			
PaH ₃	black		cubic		6.648			
β-UH ₃	black		cubic		6.6310			10.92
Np ₄ H ₁₅	black							
PuH ₂	black		cubic	<i>Fm</i> 3 <i>m</i>				10.40
PuH ₃	black		hexagonal	<i>P</i> 6 ₃ / <i>m</i> <i>mc</i>	3.78		6.76	9.61
AmH ₂	black		cubic					
Am ₄ H ₁₅	black		cubic					
Ac ₂ O ₃	white		hexagonal		4.07		6.29	9.19
Pu ₂ O ₃			hexagonal	La ₂ O ₃	3.841		5.958	11.47
Am ₂ O ₃	tan		hexagonal	La ₂ O ₃	3.817		5.971	11.77
	reddish-brown		cubic	Mn ₂ O ₃	11.03			10.57
Cm ₂ O ₃	white		cubic		5.50			
ThO ₂	white	~3050	cubic	fluorite	5.5859			10.00
PaO ₂	black		cubic	fluorite	5.505			
UO ₂	brown to black	2800 ± 200	cubic	fluorite	5.648			10.97
NpO ₂	apple-green		cubic	fluorite	5.425			11.11
PuO ₂	yellow-green to brown							
	black	~1750	cubic	fluorite	5.3960			11.46
AmO ₂	black		cubic	fluorite	5.383			11.68
CmO ₂	black		cubic	fluorite	5.372			
AcF ₃	white		hexagonal	LaF ₃	4.17		7.53	7.88
UF ₃	black	> 1140 (dec)	hexagonal	LaF ₃	4.146		7.348	8.95
NpF ₃	purple or black		hexagonal	LaF ₃	4.108		7.273	9.12
PuF ₃	purple	1425	hexagonal	LaF ₃	4.087		7.240	9.32

AmF ₃	pink		hexagonal	LaF ₃	4.067		7.225	9.53
CmF ₃	white		hexagonal	LaF ₃				
AcCl ₃	red	835	hexagonal	UCl ₃	7.62		4.55	4.81
UCl ₃	white	~800	hexagonal	C6 ₃ /m	7.442		4.320	5.51
NpCl ₃	emerald-green	760	hexagonal	C6 ₃ /m	7.405		4.273	5.58
PuCl ₃	pink		hexagonal	C6 ₃ /m	7.380		4.238	5.70
AmCl ₃	white		hexagonal	C6 ₃ /m	7.38		4.25	5.78
AcBr ₃	red	730	hexagonal	C6 ₃ /m	8.06		4.68	5.85
UBr ₃	green		hexagonal	C6 ₃ /m	7.942		4.440	6.53
α-NpBr ₃	green		orthorhombic	C6 ₃ /m	7.917		4.382	6.62
β-NpBr ₃	green		orthorhombic	Cmm	12.65	4.11	9.15	6.62
PuBr ₃	white	681	orthorhombic	Cmm	12.62	4.09	9.13	6.69
AmBr ₃	white		orthorhombic	Cmm	12.6	4.11	9.12	
ThF ₄	white	1111	monoclinic	UF ₄	13.1	11.01	8.6	5.71
					$\alpha_2 = 126 \pm 1^\circ$			
PaF ₄	reddish-brown		monoclinic	UF ₄				
UF ₄	green	960	monoclinic	C2/c	12.82	10.74	8.41	6.70
					$\alpha_2 = 126^\circ 10'$			
NpF ₄	green		monoclinic	UF ₄	12.67	10.62	8.31	6.8
					$\alpha_2 = 126^\circ 10'$			
PuF ₄	brown	1037	monoclinic	UF ₄	12.59	10.55	8.26	7.0
					$\alpha_2 = 126^\circ 10'$			
AmF ₄	tan		monoclinic	UF ₄	12.49	10.47	8.19	
					$\alpha_2 = 126^\circ 10'$			
CmF ₄	white	770	monoclinic	UF ₄				
ThCl ₄	greenish-yellow		tetragonal	I4/amd	8.473		7.468	4.60
PaCl ₄	green	590	tetragonal	I4/amd	8.377		7.482	
UCl ₄	red-brown	538	tetragonal	I4/amd	8.296		7.487	4.87
NpCl ₄	white	64.02/1137 mm	tetragonal	I4/amd	8.25		7.46	4.92
UF ₆	brown	53	orthorhombic	Pnma	9.900	8.966	5.207	5.060
NpF ₆	reddish-brown	50.75	orthorhombic	Pnma	9.91	8.97	5.21	5.00
PuF ₆			orthorhombic					

Actinide ions form complex ions with a large number of organic substances. Their extractability into these substances varies from element to element and depends markedly on oxidation state. A number of important separation procedures are based on this property. Solvents which react in this way are tributyl phosphate, diethyl ether, ketones, such as diisopropyl ketone or methyl isobutyl ketone, and several glycol ether-type solvents such as diethyl Cellosolve (ethylene glycol diethyl ether) or dibutyl Carbitol (diethylene glycol dibutyl ether).

A number of organic compounds, for example, acetylacetone and cupferron, form compounds with aqueous actinide ions (IV state for reagents mentioned) that can be extracted from aqueous solution into immiscible organic solvents. The chelate complexes are especially noteworthy and, among these, the ones formed with diketones, such as 2-thenoyltrifluoroacetone ($\text{C}_4\text{H}_3\text{SCoCH}_2\text{COCF}_3$), are of importance in separation procedures for plutonium.

Metallic State. The actinide metals, like the lanthanide metals, are highly electropositive. They can be prepared by the electrolysis of molten salts or by the reduction of a halide with an electropositive metal, such as calcium or barium. Their physical properties are summarized in Table 7. Metallic protactinium, uranium, neptunium, and plutonium have complex structures which have no counterparts among the lanthanide metals. Plutonium metal has very unusual metallurgical properties. It is known to exist in six allotropic modifications between room temperature and its melting point. One of the most interesting features of plutonium metal is the contraction undergone by the delta and delta-prime phases with increasing temperature. Also noteworthy is the fact that for no phase do both the coefficient of thermal expansion and the temperature coefficient of resistivity have the conventional sign. The resistance decreases if the phase expands on heating. Americium is the first actinide to show a resemblance in crystal structure to the lanthanide metals. It has been suggested that the interatomic distances in the actinide metals, which have been deduced from crystal structure data, indicate that $6d$ electrons are present. With respect to chemical reactivity, however, they resemble the lanthanide metals more than the metals of the $5d$ elements, such as tantalum, tungsten, rhenium, osmium, and iridium.

Solid Compounds. The tripositive actinide ions resemble tripositive lanthanide ions in their precipitation reactions. Tetrapositive actinide ions are similar in this respect to Ce^{4+} . Thus the fluorides and oxalates are insoluble in acid solution, and the nitrates, sulfates, perchlorates, and sulfides are all soluble. The tetrapositive actinide ions form insoluble iodates and various substituted arsenates even in rather strongly acid solution. The MO_2^+ actinide ions can be precipitated as the potassium salt from strong carbonate solutions. In solutions containing a high concentration of sodium and acetate ions, the actinide MO_2^{2+} ions form the insoluble, crystalline salt $\text{NaMO}_2\text{-(CH}_3\text{COO)}_3$. The hydroxides of all four ionic types are insoluble; in the case of the MO_2^{2+} ions, compounds of the type exemplified by sodium diuranate ($\text{Na}_2\text{U}_2\text{O}_7$) can be precipitated from alkaline solution. Peroxide solutions react with actinide ions, particularly M^{4+} ions, to form complex peroxy compounds in solution, and such compounds can be precipitated even from moderately acid solutions. Inorganic anions, eg, sulfate, nitrate, or chloride, are often incorporated in the solid peroxy compounds.

A great many compounds of the actinide elements have been prepared, and the properties of some of the important ones are summarized in Table 8. The binary com-

pounds with carbon, nitrogen, silicon, and sulfur are not included; these are of interest, however, because of their stability at high temperatures.

As has been mentioned, the standard techniques used in inorganic chemistry, modified in the direction of microchemical methods because of the small amounts of material available or the radioactivity of the material, are used to prepare actinide compounds. Table 9 presents an indication of the methods employed in the synthesis of some common species of actinide compounds.

Table 9. Synthetic Methods for Preparation of Some Actinide Compounds

Compound	Preparative method	Comments
hydrides	H ₂ on metals	decomposition of hydride by heating produces finely divided metal which is useful starting point for the preparation of many other compounds
oxides	O ₂ on metals or decomposition of an oxygen-containing compound, such as a hydroxide, nitrate, or oxalate	for elements with multiple oxidation states, many phases with variable composition can occur
fluorides	for the lower fluorides, HF on oxides; for higher fluorides, additional use of F ₂ or O ₂	
chlorides	Cl ₂ on metal or hydride; hydrochlorination of oxides with CCl ₄ , COCl ₂ , S ₂ Cl ₂ , BrCl ₃ or other powerful chlorinating agents (a lower form, such as UCl ₃ , may require the use of H ₂ as a reducing agent)	
bromides	Br ₂ on metal or hydrobromination of oxides	
iodides	I ₂ on metal or HI on metal	

Crystal Structure and Ionic Radii. Crystal structure data have provided the basis for the ionic radii which are summarized in Table 10. It can be noted that for both M³⁺ and M⁴⁺ ions there is an actinide contraction, analogous to the lanthanide contraction, with increasing positive charge on the nucleus.

As a consequence of the ionic character of most actinide compounds and of the similarity of the ionic radii for a given oxidation state, analogous compounds are generally isostructural. In some cases (for example, UBr₃—NpBr₃—PuBr₃—AmBr₃) there is a change in structural type with increasing atomic number, which is consistent with the contraction in ionic radius that takes place. The stability of the MO₂ structure (fluorite type) is especially noteworthy as it leads to the existence of such compounds as PaO₂, AmO₂, and CmO₂ despite the instability of the IV oxidation state of these elements in solution. The actinide contraction and the isostructural nature of the compounds constitute some of the best evidence for the transition character of this group of elements.

Table 10. Ionic Radii of Actinide and Lanthanide Elements

No. of 4 <i>f</i> or 5 <i>f</i> elec- trons	Lanthanide series				Actinide series			
	Element	Radius, A	Element	Radius, A	Element	Radius, A	Element	Radius, A
0	La ³⁺	1.061			Ac ³⁺	1.11	Th ⁴⁺	0.99
1	Ce ³⁺	1.034	Ce ⁴⁺	0.92	(Th ³⁺)	(1.08)	Pa ⁴⁺	0.96
2	Pr ³⁺	1.013	Pr ⁴⁺	0.90	(Pa ³⁺)	(1.05)	U ⁴⁺	0.93
3	Nd ³⁺	0.995			U ³⁺	1.03	Np ⁴⁺	0.92
4	Pm ³⁺	(0.979)			Np ³⁺	1.01	Pu ⁴⁺	0.90
5	Sm ³⁺	0.964			Pu ³⁺	1.00	Am ⁴⁺	0.89
6	Eu ³⁺	0.950			Am ³⁺	0.99		
7	Gd ³⁺	0.938			Cm ³⁺	0.98		
8	Tb ³⁺	0.923	Tb ⁴⁺	0.84				
9	Dy ³⁺	0.908						
10	Ho ³⁺	0.894						
11	Er ³⁺	0.881						
12	Tm ³⁺	0.869						
13	Yb ³⁺	0.858						
14	Lu ³⁺	0.848						

Absorption and Fluorescence Spectra. The absorption spectra of actinide and lanthanide ions in aqueous solution and in crystals contain narrow bands in the visible, near-ultraviolet, and near-infrared regions of the spectrum. Much evidence indicates that these bands arise from electronic transitions within the 4*f* and 5*f* shells, in which the 4*fⁿ* and 5*fⁿ* configurations are preserved in the upper and lower states for a particular ion. In general, the absorption bands of the actinide ions are some ten times more intense than those of the lanthanide ions.

Fluorescence is generally observed in actinide compounds under the proper conditions for excitation. It is observed in the trichlorides of uranium, neptunium, americium, and curium, diluted with lanthanum chloride, through the action of ultraviolet radiation.

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ACTIVATED SLUDGE. See Sewage.

ACTIVATION ANALYSIS. See Radioactive analytical methods.

ADHESIVES

Current usage defines an *adhesive* as a substance capable of holding materials together by surface attachment. The term adhesive is now considered to be a general term that includes other materials, such as cement, glue, mucilage, and paste. Although all of these terms are loosely used interchangeably, adhesive is generally becoming most widely used, and it is considered the most acceptable general term for all such bonding agents. The term *adherend* is generally used to refer to the body held to another body by the adhesive. The process of attaching one adherend to another by means of an adhesive is generally referred to as *bonding*, although other terms, such as gluing or cementing, are often used in certain branches of the industry. The final assembly of the two adherends and the adhesive is most commonly referred to as the *bond* but it is also referred to as a *joint*. The term *glue* originally referred to adhesives prepared from animal proteins, such as hides, hoofs, cartilage, and tendons. These glues were widely used in the woodworking industry, and the term glue is still generally used by the industry to include all adhesives used on wood. The term *paste* refers to certain adhesive compositions that have a characteristic plastic-type consistency with a high order of yield value and are derived by heating mixtures of starch and water and then cooling. A *mucilage* is an adhesive prepared from vegetable gums and water and is mainly used for bonding paper. The term *cement* is commonly used to refer to adhesives based on rubbers or thermoplastic resins dispersed in organic solvents and which set by loss of solvent (this is, of course, quite apart from its meaning in "portland cement"). A more complete set of definitions for these and other terms related to adhesives and their applications is given in a publication of the American Society for Testing and Materials (1).

Classification of Adhesives. The great variety of modern adhesives may be classified by several methods. A common method, based on chemical composition of the main components, is illustrated in Table 1. This system is often helpful and works well for the simpler adhesives. However, it does not adequately cover many

Table 1. Classification of Adhesives Based on Composition of the Principal Components

<i>Naturally occurring materials</i>	
	starch, dextrins, and vegetable gums
	proteins (from both vegetable and animal sources)
	a. animal (hides, sinews, bones)
	b. fish (skins)
	c. blood (whole blood or albumin)
	d. casein
	e. soybean meal (also peanut meal and other vegetable proteins)
	others
	a. asphalt
	b. shellac
	c. natural rubber (or reclaimed rubber)
	d. sodium silicate, magnesium oxychloride, and other inorganic materials
<i>Synthetic materials</i>	
	thermoplastic resins: cellulose esters and ethers, alkyd and acrylic esters, polyamides, polystyrene, synthetic rubbers, polyvinyl alcohol and derivatives
	thermosetting resins: urea, melamine, phenol, resorcinol, furan, epoxy, unsaturated polyesters

of the newer formulations in which several different components, all important to the adhesive system, are combined. Thus, some of the newer structural metal-bonding adhesives may be combinations of a phenol resin with a synthetic rubber, or with a thermoplastic resin, or even all three. Other combinations include protein-latex, or protein-blood formulations, as well as endless combinations of two or more synthetic resins, such as urea and melamine resins, or phenol and resorcinol resins. Thermoplastic resins may be formulated with other materials to produce certain degrees of thermosetting properties.

Another classification considers the main types of uses. According to this system, adhesives may be classified into: (a) *structural adhesives*, where their primary function is to hold two adherends together and produce high strength in shear, tension, or peel; (b) *holding adhesives*, where they are intended primarily for merely attaching one adherend to another and holding it in place without requiring any significant resistance to external stressing; and (c) *sealing adhesives*, where the principal function is to close a joint between two adherends to provide a seal against moisture, gases, or vapors without necessarily providing any significant strength. Obviously, many adhesive applications may require two or even all three functions. Structural adhesives are commonly used in wood and metal bonding in the fabrication of building components, such as trusses or structural sandwich panels. Holding adhesives have been widely used in labeling, packaging, and attachment of wallpaper, and wall, floor, and ceiling tile. Sealing adhesives are used to close packages for food and drug items and are also used in fabricating containers, such as the wing fuel tanks for airplanes, where the adhesive may have to contribute some structural properties as well as sealing.

Adhesives are frequently classified according to the adherends with which they are commonly used. Thus, there are paper-bonding adhesives, wood-bonding adhesives, metal-bonding adhesives, or plastic-bonding adhesives. Each type may include those where structural properties are required, as well as other adhesives where holding or sealing is more important.

Adhesives are sometimes classified according to their scale of use. Thus, industrial adhesives are those used in the fabrication of bonded products, usually on a fairly large scale, and are, therefore, consumed in rather large quantities. Household or small package adhesives, on the other hand, include special formulations developed primarily for occasional use in a wider variety of applications. The same basic chemical components may be involved, but different properties are required in each type of use. Industrial adhesives may not require long storage stability since they are commonly used soon after manufacture and must be economical. They are normally used with rather complex bonding equipment. Small package adhesives must have good storage stability before use, and since they are applied essentially by hand methods, they must be usable with very simple clamping equipment.

Statistics. Reliable figures on the production or use of adhesives are difficult to find because of the very wide variety of uses and the diversity of the industries using them. Data on uses of adhesives by chemical types are often difficult to interpret accurately because the term adhesive sometimes includes borderline applications such as bonding glass or mineral fibers in insulating batts or pads, or bonding abrasive granules in coated abrasive papers or grinding wheels.

Some useful figures on production of adhesives from synthetic resins are published annually by the U.S. Tariff Commission. These are summarized in Table 2. The production and use of adhesives has been growing rapidly since World War II. This is largely due to the use of synthetic polymers, many of which were developed for other uses and then modified and adapted for adhesive applications. One estimate, based on Tariff Commission figures, suggests that the combined tonnage of phenol, urea, melamine, and vinyl resins for adhesives has grown at an annual rate of 15 to 20 per-

Table 2. Production of Organic Adhesives^a

Type	Production (dry basis), pounds		
	1958	1959	1960
<i>Phenolic and other tar-acid resins</i>			
bonding and adhesive resins for:			
laminating (except plywood)	64,386,009	75,730,181	69,553,985
coated and bonded abrasives	12,548,309	16,207,682	14,793,403
friction materials (brake linings, clutch facings, and similar materials)	13,473,540	17,240,628	12,558,517
thermal insulation, glass fibers, rock wool	46,655,592	52,248,850	43,318,482
plywood	51,410,786	61,251,096	54,448,222
all other bonding and adhesive uses	41,364,512	63,550,542	69,328,650
<i>Urea and melamine resins</i>			
bonding and adhesive resins for:			
laminating	31,794,681	36,331,611	35,547,345
plywood	100,406,055	113,329,130	93,198,148
all other bonding and adhesive uses	11,600,174	24,525,882	27,216,315
<i>Vinyl and vinyl copolymer resins</i>			
adhesives (resin content)	47,993,976 ^b	58,184,308 ^b	59,063,195 ^b
<i>Epoxy resins</i>			
all uses other than protective coatings		23,989,168 ^b	30,778,493 ^b

^a From U.S. Tariff Commission, *Facts for Industry Series, Series 6-2-180*.
^b Sales figures.

cent between 1951 and 1959. According to Adhesive Manufacturers' Association figures, 53 million pounds of synthetic-resin adhesives went into packaging in 1950, and by the end of 1958 this annual tonnage had increased nearly threefold to 153 million pounds. During the same period, vegetable-base adhesives in packaging climbed from 226 to 250 million pounds per year, whereas animal-base adhesives dropped from 28 to 22 million pounds (2).

Advantages and Limitations of Adhesive Bonding

Adhesive bonding fulfills the need for an easy and rapid joining together of two adherends and in addition has several important advantages that are not found with mechanical fastenings, such as nails, screws, or bolts, with soldering, or with welding.

1. Certain materials that would be impossible or impractical to attach by other means can be joined. This advantage is utilized in the bonding of paper labels to cans or bottles.

2. Joining of two or more similar or dissimilar materials can be done more economically and efficiently by adhesive bonding than by other methods. The combining of many small pieces of wood into larger glued assemblies is an example of this.

3. Smoother surfaces and contours can be obtained by adhesive bonding of materials, such as brake and clutch facings or aircraft assemblies, in which rivet heads or other projections affect performance.

4. There is more efficient and uniform transfer of stresses from one member to another than with mechanical fastenings, as illustrated by modern glued-wood roof trusses, stressed-cover house panels, and helicopter rotor blades. Adhesive bonding has been particularly effective in increasing the fatigue life of assemblies by reduction of stress risers, as in rotor blades.

5. Adhesive bonding has made possible the design of new and better composite articles by taking advantage of the best properties of each of the joining materials. This is shown in the design of light but strong sandwich panels, flush doors, metal-faced plywood, adhesive-bonded rubber motor mounts, and endless combinations of wood, paper, metals, plastics, rubbers, and other materials.

6. Corrosion of joints in dissimilar metals is reduced by preventing direct metal-to-metal contact.

7. Better sealing action is provided for gases and liquids in joints than is possible with mechanical fastenings. Two examples of this are the bonding of extrusions to seal the edges of sandwich panels and the fabrication of watertight wood boats by adhesive bonding of components.

In addition, considerable reductions in weight are often possible using adhesive-bonded constructions, as in structural metal aircraft assemblies, by permitting use of thinner gages of metal which are reinforced where necessary, as around cutouts and along edges. Production costs can often be reduced by adhesive bonding as compared to conventional mechanical fastenings—for example, in certain aircraft assemblies. This is often particularly significant as the size of the assembly increases since the entire assembly may be bonded at one time and is thus cheaper than automatic riveting. However, cost comparisons of adhesive bonding with other methods of fastenings are based on many interrelated factors, including the cost of the adhesive, related processing and equipment costs, labor costs, and other factors that make it impossible to generalize on actual relative costs of the different methods.

At the same time, certain limitations of adhesive bonding, as compared to the use of mechanical fastenings, must be recognized. Generally, relative strengths with adhesive bonding are somewhat more directional than with mechanical fastening, particularly with metal-bonding adhesives. Such adhesives are very good in shear, acceptable in tension, and low in resistance to cleavage or peel. Surfaces to be bonded must be cleaner and more carefully prepared than is usually necessary for mechanical fastenings. Adhesion of a certain chemical type of adhesive is generally better for some adherends than for others. Any given adhesive application, therefore, requires a rather specific adhesive formulation and may also require special bonding conditions. At present, there is no single adhesive or bonding process that begins to meet the requirements of a truly general-purpose adhesive. It is doubtful whether such a product is likely to be developed very soon. Adhesives generally do not develop their full strength and permanence immediately, as with welded or mechanical joints, but often require appreciable time for the reactions of setting or curing to take place. Production equipment is somewhat different than for mechanical fastening techniques. Adhesive bonding requires jigs and presses to insure adequate and intimate contact of the mating adherends at the time the adhesive solidifies. Presently available adhesives, which are nearly all based on organic compounds, vary considerably in permanence in joints. Some types deteriorate as a function of time under certain conditions of service. For example some have limited heat resistance above 400°F for periods of more than a few hours. However, recent developments indicate that much more thermally stable adhesives can be produced. Finally, the present lack of reliable nondestructive test procedures for evaluating the final bond quality in production makes it necessary to practice close quality control over the entire bonding process in order to be certain of uniform bond quality, particularly in structural joints.

Recent developments in new synthetic resins and other components have made possible the development of many new, stronger, more durable, and more versatile adhesives for bonding surfaces previously difficult or impossible to bond. In addition, a great deal of experience has been gained in improved bonding techniques and new bonding equipment has been developed. Greater attention has been directed toward better designs for bonded joints. This has resulted in wider, more important, and more critical applications than were ever thought to be possible. There is good reason to believe that this development of better adhesives and bonding processes will continue at an accelerated pace in the future.

The Adhesive Joint

It is often helpful to consider an adhesive-bonded joint as being analogous to a chain of at least five links. These links include the cohesive strength of one adherend, the interfacial bond strength of the adhesive to this adherend, the cohesive strength of the adhesive layer itself, the interfacial bond strength to the opposite adherend, and finally the cohesive strength of the opposite adherend. The actual strength of the joint itself is essentially the strength of the weakest link. Two additional links may also be considered, namely the cohesive strengths of the adhesive layer itself immediately adjacent to each adherend, which may be somewhat different from the cohesive strengths of the bulk adhesive layer itself. This portion of an adhesive immediately adjacent to the adherend surface, which may be only a few molecules thick, has been referred to by Bikerman as the "weak boundary layer" (3). This layer may

be influenced by the nature of the adherend surface in any of several ways, including orientation of the adhesive molecules at the adherend surface, faults or defects in the adhesive film induced by the imperfections in the adherend, and certain specific physical or chemical interactions that are quite distinct from the actual forces of adhesion and which generally have not been adequately investigated so far. The adherends themselves may also have different cohesive strengths at the surface than are indicated by their bulk properties, as in the case of oxide coatings on the surface of certain metals.

Experience in practical adhesive bonding with a variety of structural adhesives on different adherends suggests that the weakest links are usually in the cohesive properties of the adherends or of the adhesive layer rather than the interfacial bond strengths. Thus, in well-made wood-to-wood joints the wood will generally be the weakest link. Well-made joints in aluminum will commonly fail in cohesion in the adhesive layer, often quite close to the adherend surface. These observations merely indicate the importance of considering all of the factors previously outlined. These are generally complex factors, only partially understood at the present time and must be studied much more completely and objectively before one can adequately predict the performance of a given adhesive joint. Some experimentation, using very simple chemical systems as adhesives, has begun but much remains to be done. How well the results of such work can be applied to the complex formulations actually used in typical adhesives remains to be seen.

The Nature of Adhesion

Forces of Adhesion. Although there has been much experimentation and discussion of the actual means by which one material adheres to another, this phenomenon is still not well understood. At one time, adhesion was believed to involve mainly a mechanical attachment in which the liquid adhesive flowed or was forced into pores or cavities in the adherend where it hardened and was thus anchored somewhat below the surface of the adherend. Such bonding due to interlocking is commonly referred to as *mechanical adhesion*. Although some such mechanical interlocking may occur in some porous adherends and may actually be of some value in raising the observed bond strength, it is now generally considered that actual adhesion is more probably due to chemical or physical forces, similar to those that hold the atoms and molecules of the adherends themselves together. These forces are often referred to as primary and secondary valence forces. This type of adhesion is often referred to as *specific adhesion*. At one time, the rule of thumb to explain such specific adhesion was that polar adhesives bonded to polar adherends and nonpolar adhesives bonded to nonpolar adherends but that nonpolar and polar materials were not compatible so far as adhesion was concerned. This actually meant very little since no adequate means of determining such polarity in advance was available to predict bonding properties before actual empirical trial. Numerous exceptions in practice were noted when dipole moments were taken as this measure of polarity.

Adhesion is assumed first to require actual wetting of the adherend by the adhesive so that contact in molecular dimensions is established. It is then assumed that permanent adhesion results if the interfacial boundary energy of the adhesive and adherend is lower than the sum of the surface energies of the adhesive and of the adherend. Unfortunately, means of adequately measuring these energies for the complex adhesives and adherends commonly involved are usually lacking. Suffice it to say

here that the forces of adhesion may involve either primary or secondary bonds. The nature of the forces of adhesion has been considered from a theoretical standpoint by a number of individuals and a great deal of speculation and discussion has been published. Most of this body of information is based on general physical and chemical considerations rather than on actual experimentation with adhesives themselves. One of the more concise and useful reviews by Reinhart suggests that primary bonds include electrovalent, covalent, and coordinate covalent bonds involving either the transfer or sharing of electrons between the atoms and molecules of the adhesive and adherend (4). Electrovalent bonds are probably not generally involved in adhesive bonding although the strong bond between copper and sulfur in rubber compounds has been reported to be of this type. Covalent bonds are considered to be more common in bonds of metals and inorganic materials. The bond produced by treatment of glass with a chlorosilane is believed to be of the covalent type. Coordinate covalent bonds are more typical where organic materials are involved, such as in the case of so-called hydrogen bonding of organic adhesives to materials containing hydroxyl or carbonyl groups, such as cellulose. So-called metallic bonds holding two pieces of metals together in direct contact involve the continuous movement of free electrons between atoms. On the surfaces this movement results in induced electrical forces which are equal and opposite in charge to the force field of a material close to the metal surface. Since they are opposite in charge, the two forces create a strong bond when the two materials are sufficiently close together. If such polarity were a strong factor in adhesion, the adhesive would have to have as strong an affinity for the metal or other adherend as it has cohesive strength.

Secondary bonds are the result of van der Waals forces arising from residual energies. These forces are greater for compounds than for atoms or molecules of elements. They are also greater for asymmetric molecules that have unequal electron distributions, called dipoles, than they are for symmetric molecules. These forces are said to result from orientation forces of permanent electrical dipole molecules, from induction effects of permanent dipoles on polarizable molecules, and from dispersion forces due to internal electron motions independent of the dipole moments. Attempts to calculate the forces of cohesion in materials were generally unsuccessful because the computed values were usually several times the observed strength values. The same situation apparently exists in computations of adhesive-bond quality. This indicates that much more needs to be known about the actual forces of adhesion before bond strengths can even be approximated from such theoretical considerations.

Internal Stresses. It should be noted, however, that various degrees of internal stress operate within the adhesive bond. These stresses are the result of faults that develop within the adhesive layer and vary with the adhesive composition, the bonding conditions, thermal or moisture changes in the adhesive film or in the adherends after bonding, and external loading in use, which in turn will be greatly influenced by the design or geometry of the joint. These stresses actually reduce the ultimate strength of the bond calculated from theoretical energy considerations so that the observed bond strength is always considerably lower than the calculated strengths. This suggests that much more must be known about causes of and means of relieving these internal stresses in actual bonds. Knowledge is also needed about the relationship of the geometry of the joint design and its relationship to the fundamental mechanical properties of both the adhesive and adherend before the full bonding potentials of adhesive-adherend systems can even be approached in practice.

The problem of internal stresses in adhesive films is worth further consideration. It is generally recognized that a typical adhesive must go through a fluid state in order to flow over the adherend surfaces and permit intimate contact with this adherend surface on a molecular scale. However, since such a liquid film has a rather low order of cohesive strength, it is desirable to convert this to a solid state to produce a strong bond. The process of changing from a liquid to a solid state usually results in some volume change, generally a reduction, which in itself creates internal stresses on the bond. Solvent-based adhesives lose this solvent, often rather slowly, before, during, or after the actual bonding process. The loss of solvent may cause volume changes or voids in the film, which are themselves sources of internal stress concentrations. Adhesives that solidify as the result of chemical reaction, as do the thermosetting-resin adhesives, also undergo volume changes that result in internal stresses in the bond. The magnitude of the stresses depends on the actual nature of the chemical reaction involved and to some extent upon the rate of the reaction. Pressure-sensitive adhesives probably undergo the least change in volume, but they generally have lower cohesive strength in the films than do other types of adhesive systems such as those based on thermosetting resins. If the surfaces of the adherends are relatively smooth and flat, shrinkage during bond formation is likely to be uniform, which will tend to draw the two surfaces closer together, resulting in rather thin adhesive films. Rough surfaces, on the other hand, tend to cause voids in the adhesive film and non-uniform shrinkage of the film, thus resulting in more points for internal stress concentrations to develop. Thin films generally do not flow readily during bond formation, whereas thick films are likely to be lower in cohesive strength and give weaker bonds. Therefore, there is probably some optimum adhesive film thickness for each adhesive-adherend combination, but the optimum thickness usually must be established empirically. Where the temperature of the bond must be raised in bonding, as for certain thermosetting and hot-melt adhesives, thermal expansion of both the adherend and the adhesive occurs. Their relative expansions may be quite different for a given temperature change. Cooling such bonds to room temperature after bonding will cause thermal contractions of the same order. These differential dimensional changes in adherend and adhesive layer also result in internal stresses within the bond. Thermally induced stresses in bonds also result because of changes in temperatures of the bonds during service, such as in aircraft joints alternately on the ground and at high altitudes.

Internal stresses in adhesive bonds can be reduced by several means. These include modification of the mechanical properties of the final dry adhesive film so that they more nearly approach those of the adherend. This modification may be accomplished by plasticizing a hard, brittle material to make it more flexible so that it tends to flow somewhat and relieves internal stresses that may form. Preparation of the adherend surfaces to avoid the need for variable and excessively thick adhesive films will also tend to reduce these internal stresses. Any means of avoiding inclusion of solvent in the adhesive film after bonding will also help. This can be achieved by using high concentrations of adhesives in the solvents or by drying techniques to remove as much solvent as possible before joining and final bond formation. Anything that can be done to match the thermal expansion coefficients of the dry adhesive film and the adherends, such as modification of the adhesive composition or use of special fillers, will also reduce internal stresses in the bonds and permit the user to develop a higher proportion of total theoretical strength of the adhesive bond than would otherwise be possible.

The final observed joint strength in a conventional shear or tension test will thus be much lower than the maximum adhesion as calculated from thermodynamic consideration of the forces of molecular attraction between the adhesive and the adherend. As outlined by Reinhart this theoretical maximum adhesion must be reduced by each of several factors, each of an unknown quantity, in order to account for the observed strength of an actual joint under test (4). These factors include (a) loss caused by incomplete wetting previously mentioned; (b) losses due to internal stresses within the joint; (c) losses due to defects in the test procedure itself, such as peculiarities of joint geometry, misalignment of the specimens under load, rates of loading, and similar factors. The magnitude of this third factor may be lessened or even result in a partial improvement if some of the inherent internal stresses in the bond are relieved by the test procedure.

Design of Joints for Adhesive Bonding

In order to take maximum advantage of the properties of structural adhesives, attention must be directed toward the design of the joint. In some cases it may be possible merely to replace rivets, screws, or other mechanical fastenings with an adhesive and achieve acceptable performance. In most cases, however, some changes in joint design are necessary in order to utilize the most important advantages of the adhesive and to minimize its disadvantages.

Most structural adhesives, such as are used in metal bonding for aircraft, are rather rigid, strong in shear, moderately strong in tension, and rather weak in peel or cleavage. Thus, it is normally better to design the joint for loading in shear as in an overlap joint, rather than in tension, as in a butt joint.

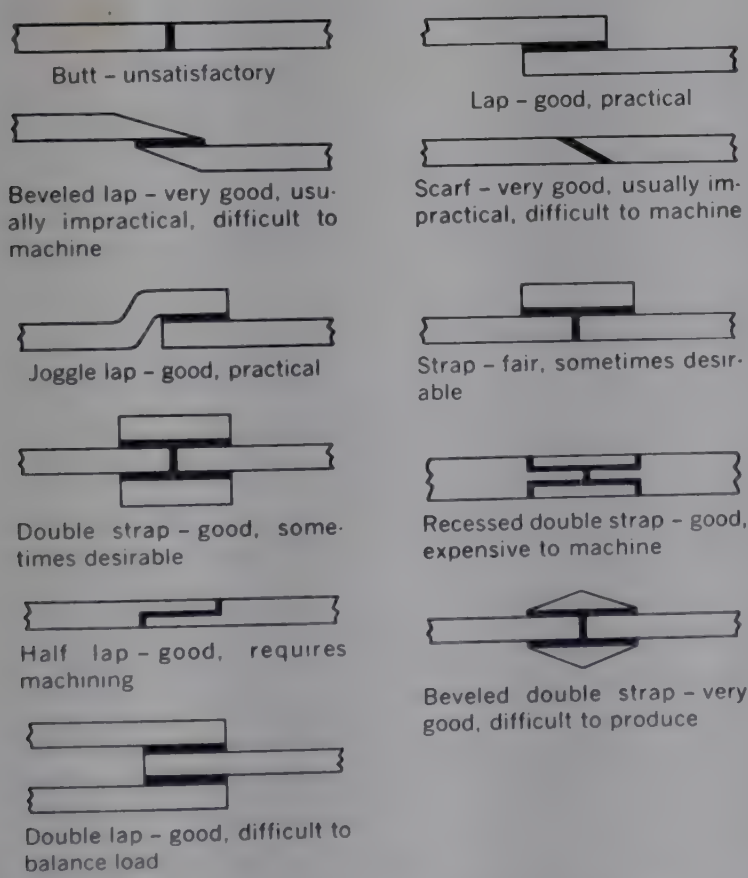


Fig. 1. Improvements in design of a simple lap joint. Courtesy Armstrong Cork Co.

Some general directions for joint design follow. (a) The bonded area should be as large as possible. (b) The maximum proportion of the bonded area should contribute to joint strength. (c) The adhesive should be stressed in the direction of its maximum strength (as in shear rather than in tension or peel). (d) Stresses in the weakest direction of the adhesive layer should be minimized (5).

Design problems in metal lap joints to be loaded in shear have probably been studied most completely at present. A simple overlap joint will not be loaded in pure shear when the two ends are pulled apart but will be subject to bending stresses that deform the adherends and the adhesive layer to varying amounts, depending on the dimensions and stiffness of the two adherends. Such bending introduces peel forces at the ends of the overlap. The strength of such a simple lap joint is directly proportional to the width of the joint. Although this strength is also proportional to the length of the overlap, this strength relationship is by no means linear and unit loads decrease proportionally as the overlap increases in length. This is caused by high stress concentrations at the ends of the lap so that the center of the bonded area may contribute very little to the observed joint strength. Various alternate designs for the simple lap joint are illustrated in Figure 1. Thus, joint strength can be improved by beveling the ends of the lap. Double lap joints and particularly a scarf joint will reduce bending and stress concentrations and thus improve joint strength. However, each improved joint design offers certain practical problems in fabrication and economy that must be considered in selecting the final joint design.

The thickness of the metal adherend also will influence the shear strength of a lap joint. If the metal is too thin, its yield strength may be lower than the shear strength of the adhesive.

Special joint design problems are encountered in bonding flexible adherends where peel forces are particularly important. Thus, in bonding thin metallic sheets or films to another metal piece, the thin material should be overlapped to place the adhesive in shear, and the overlap should be as long as possible in order to place the minimum unit shear stress on the adhesive.

Better joint designs for the assembly of corners, stiffeners, and T-sections are also possible through careful engineering analysis of the problems involved.

In some applications the joint design and the mechanical properties of the adhesive are chosen to achieve some unusual performance. In sealing the flaps on the top of corrugated fiberboard cartons for canned or bottled food products, an adhesive is sometimes chosen to produce good shear strength to insure stiffness and resistance to racking in transit and handling but with rather low tensile strength so that the flaps can be pulled up easily to open the carton for unpacking.

Another simple example of a change in joint design in changing from riveted to adhesive-bonded construction is in the attachment of an embossed metal label to a cylindrical metal fire extinguisher. The thick, flat original label with an uneven surface from embossing resulted in internal stresses in the bonded joint due to the deformation of the metal required for initial mating and incomplete wetting due to the uneven surface. Redesigning to use a thinner gage, smooth printed label that was preformed to the curvature of the cylinder resulted in more complete bonding over the joint area, less stress on the bond, and significantly improved performance in an essentially nonstructural application.

Another solution to some joint design problems is to modify the mechanical properties of the adhesive layer, so that the particular limitation of the adhesive is

minimized. Thus, it has been possible to improve peel resistance of metal-bonding adhesives. Reformulation significantly reduces peel failures, as in bonding thin metal facings to honeycomb cores in sandwich panels. Such reformulation has its limitations, however, since it also may change other desirable properties, such as resistance to heat distortion or general permanence.

Processes by Which Adhesives Develop Strength

Different types of adhesives cure or harden to their characteristic levels of strength by any of several different processes.

Air-Drying or Solvent-Responsive Types. In these adhesives, the bonding agents are dissolved or dispersed in a liquid to permit the necessary flow during application to the adherend. These systems may be solutions, emulsions, dispersions, or pastes. In all cases, the solvent must be lost from the adhesive film in order to produce the gelling or hardening by which final bond strength is achieved. The solvent may be partially lost to the air before the joint is assembled or it may be adsorbed by the adherend. The liquid used in such adhesives may be a rather complex mixture of liquids, including solvents to produce actual solubility, cheaper liquids to serve as diluents or thinners, and other solvents or thinners to control the flash point or volatility to the desired degree. In some simple systems, such as the familiar starch and dextrin glues and pastes, water is the only liquid.

Various organic solvents are needed to permit the application of rubber and various thermoplastic-resin bases. These types are common in mastic adhesives of asphalt, rubber, and similar materials used on acoustical tiles and floor tiles or for the fabrication and repair of rubber goods. A variation of this type is the solvent-reactivated adhesives. Here the adherend is coated with the adhesive in solution form and then dried to a tack-free condition for convenience in storage and handling. When ready for use, the dried film is partially liquefied on the surface by application of the appropriate solvent or dispersing agent and the bond is assembled. Typical examples are the familiar gummed paper tapes and labels or postage stamps, but more complex systems are also used in which organic solvents are used for reactivation.

Hot-Melt or Fusible Types. Any adhesive base that can be readily softened by moderate heating, without degradation of the base itself, can be melted and then applied in molten form to the adherend. Hardening or strength development can then result merely by cooling to the solid state while the bond is in contact. The earliest of these hot-melt adhesives was the original animal glue used by cabinet and furniture makers. Here the dry animal protein glue is dispersed in water at room temperature to form a stiff gel. This gel is then melted and kept molten at a temperature of 140 to 160°F, at which temperature it is applied to the adherend. Cooling to room temperature causes solidification and development of bond strength. Some more complex, newer formulations may contain thermosetting- as well as thermoplastic-resin components. These formulations may require additional heating to develop full strength after the original adhesive has been melted. Materials suitable for hot-melt application include the older waxes, as well as newer cellulose esters and ethers, the polyvinyl esters and acetals, and certain polyamides. As with other types of adhesives, various additives may be added to these hot-melt adhesives to increase tackiness, flexibility of the film, or flow properties of the film during application. Such modern hot-melt adhesives have one obvious advantage in that they contain no water

or expensive solvents that must later be removed, and many are extremely fast-setting because simple cooling is all that is required to develop bond strength. As a group, they are all thermally sensitive, and the bond can be destroyed again by reheating. These adhesives find wide application in labeling, package sealing, and book binding where the fast-setting feature makes them particularly adaptable to high-speed production.

Pressure-Sensitive Types. Adhesives of this type have a high degree of tackiness as compared to other types of adhesives. As a result, they bond almost instantaneously when slight contact pressure is applied to force the two mating surfaces together. Such adhesives have rather high cohesive strength so that despite their high degree of tackiness they can be removed from smooth surfaces without leaving an appreciable residue. When some liquid adhesives are first spread and then partially dried, they produce pressure-sensitive films that form bonds of moderate strength when mating surfaces are first brought together. An example is the neoprene-base adhesive used to bond plastic laminate sheets to wood or metal backings. However, the most important applications of pressure-sensitive adhesives are the numerous types of such adhesives deposited on paper, plastic sheets, cloth, and metal foils either by solvent casting or by calendering the molten composition on hot rolls. The adhesive composition generally consists of some film-forming elastomeric material, often one of several types of natural or synthetic rubber, and some type of resin or other material to impart the desired degree of tack, wetting power, and specific adhesion. Resins for such tack and wetting include various rosin derivatives, such as dehydrogenated rosin, hydrogenated rosin, or their esters. Terpene resins and other synthetic resins are also used as tackifiers. As with other types of adhesives, various fillers, plasticizers, and other modifiers may also be used. The actual pressure-sensitive tapes consist of several components: (a) the backing, or flexible material such as paper, textiles, plastic films, or metal foils; (b) a release coating, a resinous or plastic coating for the desired degree of adhesion between the backing and the actual pressure-sensitive adhesive (this coating must repel the adhesive sufficiently to allow unrolling without damaging the backing but must be strong enough in shear so that the tape will not fail in shear when overlapped); (c) a primer or anchor coating used mainly on plastic films and foils and frequently of an elastomer-based material; (d) the actual adhesive as described above. The various components are usually applied to the backing by knife or roller coating or calendering (6). One special requirement of many of these pressure-sensitive tapes is that they must bond instantly upon contact or under light pressure to form a bond of appreciable strength, and they must be easy to remove completely by a quick pull. This is particularly important where such tapes are used as masking tapes in painting or sandblasting operations. Particularly in masking during painting, the tape must then be pulled up completely without pulling loose any of the underlying adherend and without necessitating any significant cleaning of the adherend.

Chemically Reactive Types. This type of adhesive is characterized by the fact that it undergoes a chemical reaction in the actual bonding process. The rate of the reaction depends on the temperature at which the adhesive film is maintained. Earlier examples included the vulcanization of rubber in adhesives and the chemical modifications of protein adhesives with formalin or other tanning agents to produce greater degrees of water and moisture resistance. The principal current application of this type, however, is in the thermosetting-resin adhesives, such as the urea, phenol,

resorcinol, furan, epoxy, and melamine resins. In these adhesives, a monomer or low-molecular-weight polymer is mixed with a catalyst (or "initiator"), or in some cases additional reactants, and spread in liquid form on the adherend. Some special adhesives are available in tape form ready to insert between the adherends. The joint is then assembled and pressure is applied, and the chemical reaction, commonly called *curing*, progresses either at room temperature or at some elevated temperature, depending upon the chemical reaction involved. Such chemically reactive adhesives have limited shelf lives and liquid pot lives when prepared for use; the length of life will depend on the temperatures at which the adhesives are stored or used. An interesting recent development in prolonging the pot life of a potentially very reactive chemical curing adhesive system is the use of microencapsulation of one of the reactants, which is then dispersed in the liquid component just before spreading (see Encapsulation). When heat or pressure is then applied during bond formation, the reactant is released from the tiny capsules, and a rapid reaction occurs to produce the desired final bonding reaction. A variation on this microencapsulation technique has been reported for solvent-activated adhesive systems, in which a selected solvent is encapsulated and then released under pressure in final bonding.

Other techniques are under study for releasing the reactants for fast-setting adhesive systems through various triggering mechanisms and the use of latent catalyst systems.

The Selection of an Adhesive

At the present time there are no all-purpose adhesives that combine all of the desired properties for a wide variety of bonding applications, and it is unlikely that there ever will be such an adhesive. Therefore, adhesives must be fitted to the actual application proposed and the selection of the adhesive from the wide variety available becomes a confusing problem. From a practical standpoint, the potential user of an adhesive will wish to consider several factors in selecting the most suitable adhesive for his purpose. Obviously, he will need to know whether the adhesive will adhere adequately to the adherends involved. Once this has been established, the most important considerations will be (a) whether the adhesive meets the general levels of strength required by the design and the intended purpose of the joint; (b) whether the adhesive has the desired working properties to be practical in the manufacturing process contemplated; (c) whether the bond will have both the necessary initial strength and the desired permanence under the expected service conditions; (d) whether the cost is reasonable. The adhesive must not have an adverse effect on the adherends, such as corrosion. Since very few adhesives will possess all of the desired properties for a given application, it is usually necessary to make the best possible compromise among the various pertinent properties. Adhesion to the adherend will depend primarily on the forces of specified adhesion previously discussed.

General Levels of Strength. This involves a reconsideration of the factors previously outlined under joint design. First, a determination of the minimum levels of shear, tensile, cleavage, peel, fatigue, long-time creep, rupture, and other strength properties is required. Consideration should also be given at this point to the possible redesign of the joint, if necessary, since this might significantly affect the choice of the adhesive. The feasibility of using any adhesive as compared to other methods of fastening should also be determined.

Working Properties. Working properties include the characteristics of an adhesive that influence application, such as mixing, spreading, pressing, curing, speed of curing or rate of strength development, and convenience of cleanup afterwards. In many industrial bonding processes, the conditions that must be used are largely dictated by practical considerations, such as whether the bonding operation can be fitted into a continuous production line including several other separate operations in sequence, or by some special field installation limitations that preclude the use of any elaborate apparatus to spread the adhesive or to maintain pressure for any length of time. This is the case with many packaging operations carried out on high-speed conveyor lines, such as bottle labeling or case sealing. This is also true for attachment of gaskets, weatherstripping, sound-absorbing pads, or upholstery in automobile body fabrication. In the same way, installation of floor or ceiling tile with adhesives requires very simple but specific conditions, such as rapid and somewhat variable adhesive application and contact pressure at any of several room conditions. These working conditions often become the most important single consideration in selection of the adhesive so that adhesives without the desired working properties cannot be considered, regardless of how cheap, strong, or durable they are. The working properties of the adhesive are related closely to the equipment requirements for using the adhesive, particularly for industrial bonding. Great progress is being made in developing special factory equipment to spread, press, and cure adhesives economically and rapidly, in a variety of joints, both in batch operations and in continuous bonding. Greatest developments in equipment have probably been in packaging and in softwood plywood manufacturing. Much remains to be done however in design and construction of bonding equipment.

Permanence. One of the most important properties imparted by many of the modern synthetic-resin adhesives is the high level of permanence they can produce in properly made joints. For some applications, such as plywood for exterior or marine use or bonded metal sandwich panels in modern aircraft, the permanence of the joint is of principal importance. In such cases, a rather expensive adhesive or one requiring elaborate bonding procedures and special, expensive equipment may be necessary in order to provide the required permanence. On the other hand, some adhesive bonds are intended to be temporary, such as those used to hold parts of shoes together during manufacture before the final stitching or other mechanical fastenings are completed. In some cases, it may actually be necessary to destroy the adhesive bond readily and economically after it has served its purpose, as in label adhesives for beverage bottles that must withstand immersion in ice water for some time in use but must then be easily removed in subsequent bottle-washing operations. One of the most serious current problems in selecting adhesives for long-term and severe service applications is the lack of reliable short-term accelerated permanence tests for adhesives. This is particularly true of tests that may be applied with confidence in screening new chemical types of adhesives for which little or no service experience is yet available.

Cost. Cost is nearly always a factor in the selection of an adhesive. The cost of the adhesive as supplied by the manufacturer; the cost of labor, solvents, fillers, and other additives to prepare it for use; the cost of equipment and labor in the bonding process; and the economic loss due to rejects from defective bonds all must be considered.

In some cases, the design of the bonded article will influence the selection of the

adhesive, apart from the problem of getting the desired adhesion to adherends involved. This is particularly true where the joint design limits the working properties of the adhesive. Examples are bonds between thick masses of metals or wood that require unusually long heating periods to transfer the necessary heat to the bond lines for curing, bonds in heavy wood constructions, or bonds between dissimilar metals that may produce unusually severe internal stresses due to moisture or temperature changes in service. In such applications an adhesive that can develop the required strength and permanence at normal shop temperatures is preferred over a hot-setting adhesive.

Composition of Adhesives

While the main component of an adhesive is generally of one or more of the types listed in Table 1, the actual formulation of a practical adhesive from such a base is often a complex process, particularly for some of the newer structural adhesives.

COMPONENTS OF ADHESIVES

Regardless of the basic type of adhesive involved, a number of general components are commonly incorporated for various purposes.

The adhesive *base* or *binder* is the component of the adhesive which is primarily responsible for the adhesion forces which hold the two bodies together. The binder is generally the component from which the name of the adhesive is derived in using a classification based on composition. There may be two or more bases in some adhesives, as in a phenolic polyvinyl butyral-base adhesive often used as a structural metal-bonding adhesive.

Solvents are needed in most adhesives to disperse the binder to a spreadable liquid form. In most wood- and paper-bonding adhesives the solvent is water. In many adhesives based on synthetic resins, rubbers, and even natural gums, a variety of organic solvents are required to achieve the necessary solubility and to provide some minimum percentage of base solids.

Thinners or *diluents* are volatile liquids added to an adhesive to modify the consistency or other properties. Such liquids are usually not true solvents for the other components when used alone but are effective in diluting or thinning the composition as might be required for spray application. They provide the desired degree of volatility compatible with the open assembly conditions of use and aid in avoiding blisters and blowups in subsequent hot pressing.

Catalysts are substances which markedly speed up the cure of an adhesive when added in minor amounts as compared to the amounts of the primary reactants. Catalysts must be chosen to increase the rate of the specific chemical reactions involved in the actual adhesive base as it hardens in the joint. A good example of a catalyst is ammonium chloride, commonly used to speed up the curing or crosslinking of urea-formaldehyde wood adhesives. In this reaction, the hydrogen (oxonium) ion is the actual catalyst, but it is released gradually from a secondary reaction between ammonium chloride and free formaldehyde in the resin to produce hexamethylenetetramine and hydrochloric acid. If free hydrochloric acid were added directly to the resin before spreading, the hardening or curing reaction would be so fast that the adhesive would gel before it could be spread. The indirect reaction is therefore used. Buffers, or retarders, such as ammonia or calcium phosphate, may also be added to control the acidity and hence this curing reaction.

Hardeners are substances or mixtures of substances added to an adhesive to promote or control the curing reaction by taking part in it. That is, a hardener is an actual chemical reactant in the curing reaction as compared to the catalyst which does not react directly but merely controls the rate of reaction. A good example of a hardener is paraformaldehyde commonly used with resorcinol-formaldehyde wood adhesives. In this case the resin is of the Novolak type, being deficient in formaldehyde in order to provide some useful storage life for the reactive resin. In order to provide the means to complete the chemical curing or crosslinking of the resin during final bond formation, the additional formaldehyde is added at the time of final mixing and application. This formaldehyde then reacts with the resin to complete the resin condensation normally completed by the resin adhesive manufacturer with less reactive resins. Aqueous formalin could be used for this purpose but it dilutes the resin, and the fumes are often offensive in actual use in large-scale bonding operations. Therefore, paraformaldehyde in powder form is commonly furnished as a separate component to be added in the prescribed amount at the time of final mixing.

Fillers are relatively nonadhesive substances added to an adhesive to improve its working properties, permanence, strength, or other qualities. These materials are generally intended to do something useful and not merely reduce cost. Examples are English walnut shell flour or pecan shell flour which are commonly added to many synthetic-resin wood adhesives to improve their spreading properties on conventional roll spreaders or to control excessive adhesive penetration into certain porous woods. Metallic and inorganic fillers, such as aluminum powder, alumina, or china clay, are often added to epoxy-resin adhesives as fillers to improve viscosity and spreadability. They can also alter the thermal expansion coefficient of the cured adhesive film in order to reduce stresses between the adherend and film due to excessively different thermal expansion and contraction characteristics.

Extenders, on the other hand, are substances generally having some adhesive action. They are added to an adhesive to reduce the amount of primary binder required per unit area and thus reduce the cost of the actual joint. Examples are wheat flour commonly added to urea-formaldehyde wood adhesives to reduce glue-line costs. The flour is often added to the binder in proportions of 1:1 on a solids basis by merely physical mixing plus some additional dilution with water to the desired viscosity.

Preservatives are agents added to certain adhesives to retard or prevent decomposition by microorganisms, either while the adhesive is being stored or applied or during service of the completed bond. These agents are usually most important in formulations containing carbohydrates or proteins, such as flour, starch, casein, or animal proteins that are readily attacked by mold, fungi, or bacteria. Preservatives include inorganic materials, such as copper or mercury salts, and many newer organic compounds, such as organic mercury compounds, and the various chlorinated phenols.

Fortifiers, a term not yet generally accepted, are materials which are added to an adhesive binder primarily to improve the permanence of the resultant bond. They may be binders or at least have some distinct adhesive value. An example is the addition of resorcinol along with paraformaldehyde to a urea-formaldehyde wood glue to improve the resistance of the resultant joints to weathering or exposure to other severe conditions. In this case the resorcinol and formaldehyde added at the time of use are assumed to react chemically to produce a sort of resorcinol-urea-formaldehyde resin system. Melamine-formaldehyde resins are also added to urea resins at the time of use for the same purpose.

A *carrier* is usually a thin fabric or foil used to support adhesive composition in order to provide a dry film adhesive. An example of this is the thin paper film used to support the phenol-formaldehyde resin in the conventional phenol-resin film glues. Another example is the use of glass cloth or even cheesecloth to support some of the newer structural metal-bonding adhesives based on phenol and epoxy resins, or of phenol and vinyl butyral resins. It should be noted, however, that some film adhesives are unsupported and thus have no carrier.

SOME TYPICAL ADHESIVE COMPOSITIONS

There are literally thousands of adhesive formulations used at present and the number is growing rapidly. Obviously, the compositions of some of the most interesting newer adhesives are not revealed publicly although many are covered by existing patents. As with other proprietary products consisting of a number of components the success of the adhesive composition may often depend on special techniques in mixing that are often not divulged by the adhesive formulator. Hence, making adhesives from the basic components is usually not a simple matter of following a prescribed recipe. This is particularly true in attempting to describe the making of a pressure-sensitive tape adhesive system.

The following examples are cited merely for illustrations, recognizing that these are the simpler, often older compositions, and that all directions and precautions could not be included to guarantee complete satisfaction from the information cited. In the case of synthetic-resin binders, only the type can generally be indicated, but in many cases several different resins of this general type could possibly be used. The reader should again recognize that the actual joint quality will depend both on the adhesive composition and on the way in which it was compounded and then used in the bonding process.

Animal Glue. Animal (hide) glue is usually available in powdered or ground form and in a number of different grades. A typical formulation for edge-gluing lumber and assembly of furniture is prepared by adding 100 parts by weight of dry animal glue (J-2 grade of Federal Specification MMM-A-100) to 225 parts of water and allowing it to stand for 1 hour at room temperature. The mixture, which will swell to a stiff gel, is then warmed to 140–150°F in a water jacketed kettle and applied while warm to the substrate at room temperature. Initial strength is then developed on cooling (see Gelatin and glue).

Casein Glue. The formulation of one of the earliest practical casein glues for woodworking, which is still in use, can be found in Table 3 (7).

Table 3. Casein Glue Formulation

Ingredients	Parts by weight
casein	100
water	150–250 (depends on ash content of casein)
hydrated lime	20–30
water	100
silicate of soda (40° Baumé silica/soda ratio of 3.25:1)	70
water	30–50

This is a wet-mixed casein glue which hardens at room temperature. The essential principle is to dissolve or disperse the casein in caustic soda (produced indirectly here from lime and sodium silicate). This is modified by forming a calcium derivative by action with lime to produce some moisture and water resistance. Dry-mix casein glues, requiring only the addition of a specified amount of water, are now available. In these glues the caustic soda is produced by interaction of specially selected dry chemicals that are unreactive until water is added to the mix. Calcium hydroxide, together with any of a great number of sodium salts, has been used for dry-mix casein glues. The sodium salts may include the fluoride, phosphate, sulfite, oxalate, and many others (8). In the dry-mix formulations the casein powder is usually coated with a low-cost mineral oil to reduce the rate at which water is adsorbed on mixing and to provide more complete mixing of the other chemicals before the action on the casein begins.

Urea-Formaldehyde Resin Adhesives. A large number of different urea-formaldehyde resins (see Aminoplasts) are available to the wood industry, including those made at different mole ratios of urea to formaldehyde, different solids contents in aqueous dispersions, and as spray-dried powders. A usable formulation for bonding hardwood plywood is presented in Table 4. This is a flour-extended formulation.

Table 4. Urea-Formaldehyde Resin Adhesive Formulation

Ingredients	Parts by weight
wheat flour (soft, clear, winter wheat)	100
water	100
<i>stir for 10 min</i>	
urea-formaldehyde resin (spray-dried)	100
<i>stir until smooth</i>	
ammonium chloride	0.5
water	55

This adhesive is cured at 240–260°F platen temperatures for 8 minutes for a 3/16 inch thick panel.

The ammonium chloride is a simple catalyst system. The literature describes many combined buffer-catalyst systems for urea-resin glues. The principal factor here is to provide sufficient hydrogen (oxonium) ion to catalyze the crosslinking of the resin and still provide a usable working life for the adhesive.

Urea-resin adhesives can also be formulated for curing at normal shop temperatures of 70°F or higher. In this case a larger proportion of, or a more active, catalyst is needed. The same basic resin-flour formulation in the example may be used for curing at room temperature by increasing ammonium chloride content to 2.5 parts.

Phenol-Formaldehyde Resin Adhesives. These adhesives are used primarily for bonding hardwood or softwood plywood for exterior use. The most widely used adhesives in the softwood plywood industry are highly alkaline phenol resins in liquid form, dispersed in water and used without additional catalysts or hardeners (9,10).

These basic resins are often extended with dry soluble whole blood, ground wood bark fractions, or residues from furfural hydrolysis of agricultural materials. Such extension may require addition of more caustic soda or some cooling at moderately elevated temperatures (see Phenoplasts).

Starch Adhesive for Nonweatherproof Corrugated Board. This adhesive is intended for bonding a corrugating medium of kraft paper to a kraft liner sheet in a

Table 5. Starch Adhesive Formulation

Ingredients	Parts by weight
water	854
bentonite clay	10
<i>agitate</i>	
corn starch	80
<i>agitate</i>	
caustic soda	
(in 3 gals of water)	13
<i>agitate</i>	
water	1,220
corn starch	505
borax	17
<i>mix</i>	
formaldehyde	1 quart

continuous high-speed bonding operation on commercial equipment (11) (see Starch). Table 5 gives the formulation for this adhesive.

Epoxy-Resin Adhesive for Metal Bonding. Because of the large number of different epoxy resins (see Epoxy resins) and the large number of amine and anhydride curing agents available, it is difficult to select any simple example. Table 6 gives an experimental formulation found to be quite satisfactory for bonding aluminum to aluminum at normal room temperature (12).

Table 6. Epoxy-Resin Adhesive Formulation

Ingredients	Parts by weight
epichlorohydrin-bisphenol resin	100
polysulfide elastomer	10
milled glass fibers, 1/32 inch	10
dimethylaminoethyl alcohol	4
triethylamine	4

Phenol-Epoxy Resin Metal-Bonding Adhesive. These adhesives have shown good resistance to thermal ageing on aluminum-to-aluminum joints at temperatures up to 450°F. The experimental formulation in Table 7 is an example of commercial types (13).

Table 7. Phenol-Epoxy Resin Adhesive Formulation

Ingredients	Parts by weight
phenol resin (Durez 16227)	12.5
phenol resin (Bakelite BV9700)	3.3
epoxy resin (Epon 1007)	2.0
1-hydroxy-2-naphthanoic acid	0.2
<i>n</i> -propyl gallate	0.2
ethyl acetate	2.0

This adhesive is precured at 200°F for 30 minutes and then cured at 320°F for 30 minutes.

Polyvinyl Acetate Emulsion Adhesive. These adhesives are widely used for bonding wood in furniture assembly and fabrication. They are also useful for bonding paper and as general-purpose household adhesives. As a type they have evolved from some earlier versions, one of which is given in Table 8 as an example of the general composition (14) (see Vinyl compounds, resins, and plastics).

Table 8. Polyvinyl Acetate Emulsion Adhesive Formulation

Ingredients	Parts by weight
polyvinyl acetate emulsion (Du Pont 81-900)	145.5
50% dibutyl phthalate-50% Arochlor plasticizer	4.5
10% aqueous solution of vinyl methyl ether-maleic anhydride copolymer (0.7 sp viscosity)	125.0

Phenol-Butyral Adhesive for Metal Bonding. This type of formulation was one of the earlier types for structural bonding of aluminum to aluminum and is still useful where temperatures less then 250°F are encountered in service. Table 9 presents this formulation.

Table 9. Phenol-Butyral Adhesive Formulation

Ingredients	Parts by weight
phenol-formaldehyde resin (Bakelite BV9700)	100
polyvinyl butyral resin (Butvar H-1935)	100
maleic anhydride	10
methyl alcohol	230
methyl ethyl ketone	230

This formulation is suitable for brush application. For spraying, it may be thinned to a solids content of about 10 percent by adding additional methyl alcohol and methyl ethyl ketone in equal proportions by weight. Bonds may be pressed at 320°F for 20 minutes.

Rubber-Base Adhesives. One formulation (A) for bonding rubber to metals is presented in Table 10 (15). This adhesive is cured at 200°F.

Table 10. Rubber-Base Adhesive Formulation A

Ingredients	Parts by weight
cyclized rubber (Pliolite)	20
benzene	80
paraphenylene diisocyanate	2-4

Another system for bonding rubber to steel consists of first priming the steel with 100 parts by weight of an alcohol solution of a phenol-formaldehyde resin (Bakelite XR5948) and suspending 40 parts thermatomic carbon in 100 parts of ethyl alcohol, which is added to the resin solution. This mixture is coated on the metal and air-

dried. A rubber stock consisting of 100 parts pale crepe rubber, 4 parts of tetrachloroquinone, and 4 parts of hexamethylenetetramine is then rolled onto the primed metal and heated in live steam for 2 hours to cure the system (16).

A rubber-base adhesive (formulation B) for can sealers and masking tapes is described in Table 11 (17). This is used as a general-purpose adhesive at room temperature. It is of the solvent-release type.

Table 11. Rubber-Base Adhesive Formulation B

Ingredients	Parts by weight
milled, stabilized, amorphous rubber	
hydrochloride	100
hydrogenated methyl abietate	200
acetone	221
benzene	221

Adhesive for Bonding Leather and Shoe Parts. An adhesive for this purpose is described in Table 12 (18). The mixture is milled on a differential roller mill. It is applied to both surfaces, air-dried, and pressed for 15–60 seconds at room temperature.

Table 12. Adhesive Formulation for Bonding Leather

Ingredients	Parts by weight
butadiene–acrylonitrile polymer (Hycar OR)	100
vinyl chloride–acetate copolymer (Vinylite VYHF)	100
sulfur	2
stearic acid	1.5
zinc oxide	5
calcium silicate	20
butyl 8 (accelerator)	0.25
methyl ethyl ketone	800

Adhesive for Bonding Fabrics and Leather. The formulation given in Table 13 is milled on a rubber mill and is intended for brush spreading, air drying, and pressing at room temperature (19).

Table 13. Adhesive Formulation for Bonding Fabrics and Leather

Ingredients	Parts by weight
polymerized chloroprene	1.25
magnesium oxide	0.063
zinc oxide	0.05

Adhesives for Bonding Paper Containers. A formulation intended for hot-melt application and rapid bonding of paper containers is described in Table 14 (20).

Table 14. Adhesive Formulation for Bonding Paper Containers

Ingredients	Parts by weight
polyvinyl acetate	70
dammar gum	30

These are kneaded together at 250–350°F for 50–60 minutes and are then applied while hot to the paper. The adhesive hardens on cooling.

Asphalt Base Adhesive. An earlier heat-setting asphalt binder for cementing felt to car bodies, which may set from 100 to 165°F, may be brushed or sprayed into position. Its composition is given in Table 15 (21).

Table 15. Asphalt-Base Adhesive Formulation

Ingredients	Percentage
equal weights of asphalt and coumarone-indene or asphalt (low in asphaltenes)	40–50
soap emulsifier	0.8–1.2
clay	1.3
rubber latex	6–9

The Bonding Process

The final quality of any adhesive bond depends both on the quality of the adhesive used and the care with which the bonding operation is conducted. Because of the great complexity of possible adhesive compositions, adherends, and service requirements, the exact bonding conditions for any given application should be prescribed by the adhesive supplier with adequate knowledge of the intended use. However, certain general factors in the bonding process are common to a great many adhesive applications regardless of the type of adhesive or bonded joint involved.

Preparation of the Adherends. In many adhesive applications, such as the use of pressure-sensitive cellophane tapes for wrapping packages, the adherend must be bonded without any previous surface treatment. In such cases, the adhesive must be so formulated that it has the necessary specific adhesion to the adherend without such treatment. In many other applications, however, the adherend must be modified by mechanical or chemical treatment prior to bonding. Machining of rigid adherends, such as metals or wood, may first be necessary to provide flat and true surfaces for proper mating of the two surfaces. Machining also permits the desired wetting by the adhesive so that a thin adhesive film can adequately bridge over both surfaces. Such mechanical surfacing may also remove surface oxides or various types of contamination that might interfere with adhesion. Light sanding of plastic surfaces, particularly those molded or pressed under high temperatures and pressures, is often of great value in improving adhesion. This is probably due to exposure of a fresh surface of higher surface energy for better specific adhesion rather than to mechanical roughening to improve mechanical adhesion, or keying, as was once supposed to occur. Other special means of activating certain adherend surfaces for bonding include ultraviolet irradiation, flame treatments, and electron bombardment.

Many adherend surfaces, such as metals, can be improved for adhesive bonding by some chemical treatment. This may be simple removal of grease, oil, and other contamination by solvent immersion, vapor degreasing, or detergent baths, or it may involve acid or alkaline etching or electrolytic procedures that chemically modify the metal surface. These chemical modifications may promote better specific adhesion and improve the properties of the adherend by removal of metallic oxide coatings of low cohesive strength or by increasing the corrosion resistance of the metal at the adhesive interface. There is some evidence available which suggests that the metal sur-

surface preparation, such as by chemical treatments, also influences the resistance of certain adhesive systems to heat ageing at elevated temperatures (22).

Certain species of wood, particularly those containing appreciable amounts of oily or resinous extractives, may be improved in gluing ability by solvent or alkaline surface treatments prior to gluing. All such surface treatments must be carefully chosen to avoid undesirable interferences in subsequent bonding, such as effects on the catalyst systems used with chemically reactive adhesives.

An interesting recent application of chemical treatment is one devised for adhesive bonding of polytetrafluoroethylene plastic surfaces by treatment with sodium. Solutions of sodium metal in liquid anhydrous ammonia have been used and more recently a treatment in a 1:1 molar complex of sodium and naphthalene in an excess of tetrahydrofuran has been described (23).

Preparation of the Adhesive. This may involve dissolving or melting solid adhesives, thinning liquid adhesives, or adding a variety of catalysts, hardeners, fillers, extenders, plasticizers, fortifiers, and other components as directed by the adhesive supplier. Obviously, failure to follow instructions properly may result in an adhesive that is incapable of consistently producing bonds of adequate quality.

Application of Adhesives. Adhesive may be applied to the adherend surfaces by brushing, roller coating, or spraying of liquid adhesives; by roller or knife coating of molten adhesives; by simply laying on a film or sheet of dry adhesive; or in the form of pressure-sensitive tapes. The supplier's recommended amount of adhesive should be applied uniformly over the entire area. Special chemically reactive adhesive systems may require application of one component, such as a thermosetting resin, to one surface and another component, such as a catalyst or a reactivating solvent, to the other surface so that the mixing will occur when the two surfaces are assembled. Some reactive systems, such as highly exothermic epoxy-resin formulations, may best be applied by combining the resin and catalysts from separate containers just at the point of application to the adherend or by double-spray application of the two components directly to the adherend surface so that mixing occurs at the very moment of application. This process permits the use of reactive mixtures that would otherwise harden almost immediately in the pot.

Assembly or Air-Drying Periods. Some adhesives that develop strength rapidly, such as by chemical reaction of thermosetting-resin adhesives or cooling of molten adhesives, require immediate assembly of the two adherends after application of the adhesive. Other adhesives, such as thermoplastic-resin or rubber solutions in organic solvents, may require fairly long periods of open assembly or air drying to permit solvents to volatilize. This may be necessary to develop the tackiness required to produce adhesion on contact with pressure-sensitive liquid adhesives or to avoid blisters and blowups in the resultant assembled bonds when subsequent hot pressing is done. Many conventional woodworking adhesives require a certain period of closed assembly after the adhesive has been applied and before bonding pressure is applied during which time the two adherends are placed together in direct contact. This permits some partial loss of solvent into the wood and some chemical reaction in the case of thermosetting-resin adhesives. It results in an increase in consistency of the adhesive layer and helps prevent excessive squeezeout when pressure is applied. The actual length of such assembly and air-drying periods is generally decreased as the temperatures of the air and the adhesive layer increase due to acceleration of the reactions involved and greater volatility of the solvents at higher temperatures.

With some metal-bonding adhesives the release of solvent is so slow at normal shop temperatures that coated adherends are heated in ovens or on press platens before or after assembly and before pressure is applied. With certain adhesives such preheating is also useful to cure partially or to polymerize the adhesive for more desirable flow during subsequent bonding under pressure. This technique is often referred to as precuring.

Bonding Pressure and Temperatures. After the liquid adhesive has reached the optimum consistency on the adherends, bonding pressure must be applied to the assembled joint. The pressure must be adequate to cause the two surfaces to come together in uniform contact, to permit liquid adhesives to flow out uniformly over the surfaces, and to work out air bubbles in the film. With pressure-sensitive or other fast-setting adhesives, pressure can then be immediately released. In slow-setting adhesives, such as certain thermosetting-resin adhesives, pressure must be maintained until chemical reactions, cooling, or other processes have proceeded to the point where adequate bond strength has been developed. Temperatures during the pressure periods will be determined by the type of mechanisms involved in strength development, as previously discussed. Molten or other thermoplastic adhesives may require some cooling under pressure. Chemically reactive or drying adhesives may benefit from increases in temperature while under pressure. Heated press platens or high-frequency electrical heating can be used for this.

Conditioning after Bonding. Certain fusible adhesives that are hot-pressed, such as thermoplastic resins, may require cooling below a certain temperature before release of pressure. Many thermosetting-resin and nonresin adhesive systems may not have developed full strength when pressure is removed. These systems must be conditioned for an additional period to permit further strength development before machining or other later operations that might otherwise damage the partially completed bond. With certain thermosetting resins, bonded panels may be tightly stacked on removal from the hot press so that the residual heat continues the curing while some pressure is retained from the weight of the stack of panels. This technique, known as hot stacking, is commonly used with phenol-resin adhesives in the plywood industry. Conditioning of bonded joints at normal shop conditions also permits equalization of temperature and moisture in adherends and adhesive films and thus relieves internal stresses before subsequent manufacturing operations.

Some Important Adhesive Applications

The number of uses for adhesives is very great, ranging from some industrial processes using tremendous total volumes each year to minor assembly operations that require small quantities, but nevertheless are very important from the standpoint of the end product. The following section merely highlights a few selected applications.

Paper Adhesives. Paper bonding and related packaging applications represent one of the largest uses of adhesives at the present time. Adhesive bonding of envelopes, bags, cartons, gummed paper labels, and stamps is familiar to all. Earlier adhesives in these fields were formulated from hydrolyzed starch (dextrin), gum arabic or gum tragacanth, and certain modified casein or animal protein bases. Most of these were dispersed in water, and they developed strength by drying. Large quantities of sodium silicate and starch adhesives are used in bonding the paper liners to core components of corrugated fiberboards and laminated paperboards for pack-

aging. Although these adhesives gave adequate strength for many applications, they often lacked the resistance to moisture and water required for overseas packaging. To improve these shortcomings, newer adhesives have been developed based on polyvinyl alcohol or acetate, starch fortified with polyvinyl acetate, and resorcinol or urea resins. Resorcinol-modified starch adhesives are a recent development for corrugated fiberboards with improved wet strength.

Hot-melt adhesives, based on polyvinyl esters and acetals or microcrystalline waxes, are finding broad applications in the paper field in the fabrication of milk cartons, heat-sealed labels, and in bookbinding. In bookbinding, the hot-melt adhesives have greatly speeded up the binding process and have eliminated the long drying periods which animal glues required for removal of water after binding. These drying periods slowed up the trimming of the pages and completion of the books. Before repulping the excess paper trimmed off the book pages after bonding, the hot-melt adhesives must be completely removed so that the properties of the new pulp are not adversely affected.

Pressure-sensitive tapes with cloth, paper, and transparent film backings and various rubber and resin adhesive systems find wide applications in the sealing of cartons and shipping cases of paper and fiberboard. Recent high-strength tapes with glass-fiber or nylon threads in the backing provide strong bindings that can be used in place of steel strapping around heavy corrugated-fiberboard shipping cases. These tapes are superior to steel straps because they not only provide the necessary tensile strength and are easier to apply but they also prevent wearing and crushing of the fiberboard. They do this by distributing stresses over the entire bond area rather than concentrating them at corners and edges, as do steel straps.

Rapid-setting, carton-sealing adhesives based on sodium silicate or starch continue to find wide application in packaging. New paper products are now made possible by using adhesives of various resin and rubber bases to combine metal foils, polyethylene, and other plastic films with high-strength or wet-strength paper to make superior case liners, multiwall shipping bags, vapor barriers for building construction, and other items.

Wood Adhesives. Historically, the bonding of wood was one of the first uses for adhesives. Accounts of veneered wood and other glued-wood assemblies date back to the Egyptian Pharaohs. Wood bonding is a very important means of improving the utilization of our wood resources. It is one of the largest volume uses of adhesives, particularly in the softwood plywood industry of the Pacific Northwest where an estimated 185 million pounds of dry adhesives was used in 1959. The older adhesives for wood were based on materials of natural origin beginning with the hide glues from animal protein by-products and then vegetable starch, casein, soybean, and blood adhesives. Although each of these types is still used in fairly large quantities, the newer synthetic-resin adhesives have been replacing many of these natural-base adhesives, particularly in certain applications. The principal uses for animal adhesives (hide glues) are in edge gluing of lumber for furniture and in the assembly of furniture. Polyvinyl resin emulsion adhesives have made important advances in these areas. Casein adhesives are used mainly for laminating heavy structural timbers for interior use in churches, schools, field houses, and commercial buildings. Soybean and blood adhesives are used primarily for bonding interior-type softwood plywood. Starch adhesives are still used to a limited extent in hardwood plywood for interior use but have been largely replaced by urea-resin adhesives which are often

extended with wheat flour for greater economy. Phenol resins are used primarily for exterior-type softwood plywood whereas resorcinol resins are used mainly for structural laminates for severe service, such as bridge timbers, crossarms, and exposed structures and boats, and in fabrication of glued wood components, such as trusses and prefabricated wall, roof, and floor panels for buildings. Melamine resins are primarily used to improve the durability of urea-resin adhesives in hardwood plywood for exterior service as in boats, a rather limited use at present.

There are a number of important new uses for adhesives, particularly in the lumber industry, that are under development or in early production trials and that promise to increase the use of adhesives for wood very significantly in the next few years (24). These involve either the combining of many smaller pieces of good-quality wood into standard sizes of panels for greater economy of use through edge and end gluing or the overlaying of lumber or plywood with special papers, hardboards, and metal or plastic sheets and foils to improve surface properties. Another growing use of adhesives is in the bonding of sheets of plywood, hardboard, or fiberboards to wood frames to produce high-strength, durable, and economical unitized panels for building components. Although each of these new products can be bonded satisfactorily with conventional wood adhesives, most of these adhesives are not readily adaptable to the economical large-volume production anticipated. There is great interest in the potentials of some of the new types of adhesives being developed for bonding other materials such as metals and plastics. Of particular current interest are certain of the rubber-base contact-setting adhesives originally introduced for bonding plastics and metals to plywood and other wood-base cores for interior use.

Metal-Bonding Adhesives. Largely because of the great importance of adhesive-bonded constructions in the aircraft and missile fields and the critical value of these fields in the Cold War period, some of the most interesting and advanced technology in the entire adhesives industry has developed in structural metal bonding. There is every reason to believe that these efforts will continue to expand, and to expect that much of the basic information in this area will greatly stimulate other developments in the adhesives field generally. Modern aircraft structures, as in supersonic planes and missiles, place great emphasis on most of the advantages cited earlier for adhesive bonding techniques—including the need for smooth aerodynamic surfaces free of projections, the very efficient distribution of stresses from one member to another, the reduction in stress concentrations common to conventional mechanical fastenings, and the reduction in weight by stiff, rigid sandwich panels of thin metal skins bonded to lightweight cellular cores of metal or reinforced plastic honeycomb cores. This is one area where the economics of adhesive bonding was not the main obstacle to their trial and use. Extreme performance requirements could often be met best by adhesive-bonded components and thus spurred on the development of a number of novel adhesive systems of new chemical nature of which the epoxy-resin adhesives are the most familiar at present.

Before World War II some metals, primarily aluminum and cold-rolled steel, had been bonded to wood with protein-rubber latex adhesives in a water dispersion. More recently the synthetic rubber-base, contact-bonding adhesives have been used for this purpose. These were essentially semistructural applications primarily for interior applications or for protected exterior uses. During World War II considerable development of new high-strength metal-bonding adhesives took place for limited applications in aircraft uses. At first these involved bonding aluminum to wood but

later bonding aluminum to itself. The earlier resin adhesives were essentially modifications of the conventional phenol-resin adhesives used for wood by incorporation of neoprene or nitrile rubber or with certain thermoplastic resins, primarily polyvinyl, butyral, or acetal. Such modification was necessary to reduce the excessive rigidity and brittleness of the adhesive layer and to accommodate internal stresses in the joints caused by differential dimensional changes in the metals and wood. These dimensional differences are the result of temperature and moisture changes during service. The earlier adhesives, based on phenol-resin modifications, required curing at 300°F or higher. After World War II the early epoxy-resin adhesives were developed, some of which can now be cured at normal shop temperatures.

The earlier metal-bonding adhesives, based on combinations of phenol resins and rubbers or thermoplastic resins, were used in solution form and problems were encountered in eliminating from the resultant joint residual solvent bubbles which reduced uniformity and joint strength. This has fostered the further development of film-type adhesives of the same general composition which only require insertion between the adherends and then hot pressing.

As service conditions for aircraft became more severe, particularly the temperature requirements, new metal-bonding adhesive systems were developed. The phenol-nitrile and phenol-epoxy combinations have generally been most promising for use at temperatures up to 500°F for periods up to 200 hours or so. Such high-temperature service in aircraft, involving primarily new corrosion-resistant steel alloys rather than aluminum, introduces problems of thermal softening as well as thermal degradation of the component polymers. The B-58 (Hustler) supersonic bomber of the Air Force utilizes 4500 square feet of bonded panels and requires approximately 900 pounds of adhesive per plane. Such a construction is expected to withstand 30,000 hours of service at 325°F. Some of the newer planes have significantly higher temperature requirements. This introduces severe requirements for adhesive performance that will be difficult to meet. Some organic adhesives based on phenolic and silicone-phenolic systems are said to be promising for use at 1000°F for short periods. Work is in progress on semiorganic adhesives obtained by reaction of newer heat-stable organic polymers with inorganic reagents such as arsenic compounds. Some authorities consider that structural adhesives for performance for 1000 hours at 500°F in steel joints will be feasible soon. Other interesting work is in progress to develop inorganic and ceramic-type adhesives, based on modifications of ceramic frits, for even higher temperature performance.

Along more conventional lines, some of the present metal-bonding adhesives are being used to bond porcelainized steel to hardboard and other backings and to a variety of insulating cores for exterior building panels.

The automobile industry is beginning to use large amounts of structural adhesives in body fabrication to replace spot welding for much the same reasons that the aircraft industry uses adhesives. A current use is in bonding inner and outer shells of metal stampings for hood and trunk lids. The assembly operation is entirely automated and consists of the application of 80 to 100 spots of a special viscous adhesive by controlled ejector valves to the metal in its original oily condition. The panel assembly is mechanically crimped around the edges and a few spot welds are made to hold the panel together temporarily. Panels are subsequently processed through metal cleaning systems, primer dips, and bake oven cycles and finally the finish color coat and drying oven cycles. The adhesive is cured to its final state during the baking of the primer.

Advantages of the new bonding process include elimination of sound deadener pads and spot weld patterns on the final surface of the finished panel. Corrosion of the panel is also reduced by the sealing action of the adhesive system.

A pump manufacturer claims to have reduced rejects very significantly by adhesive bonding of three separate metal die castings to form one complicated part. This replaces a one-piece casting which, because of its intricate shape, resulted in excessive blowholes in the castings. Tubular joints of metal are now adhesive-bonded for scaffolding, bicycle frames, and lines for refrigerants, gas, and hydraulic fluids. Epoxy adhesives are used to bond carbide tips to metal for cutting tools. The pressure bulkhead of a liquid ammonia tank in a research rocket aircraft has been bonded and sealed with a special metal-bonding film adhesive. A special epoxy-resin adhesive has been used to assemble water tight, lightweight metal containers for shipping, housing, and storing complex electronic and mechanical gear for the armed services.

Brake and Clutch Bonding Adhesives. Two of the major automobile manufacturers have been bonding brake linings to drums since 1947. The principal adhesive system is apparently a phenol-nitrile rubber type used either in liquid or film form and heat-cured. Advantages include greater life because of the absence of rivet heads and lower production costs (25). Clutch facings and facings for automatic transmissions, where parts are immersed continually in warm oil, have also been bonded in recent years.

Printed Circuits. One of the principal processes for manufacture of printed circuits for electronic components involves the bonding of a copper foil to a phenolic-laminate panel using primarily vinyl-phenolic adhesives. Epoxy and nitrile-phenolic adhesives are also used. The circuit pattern is then applied to the copper film as a protective coating and the excess copper etched away. Various electronic components are later inserted through holes in the remaining metal and all soldered to the copper foil by a short dip in molten solder. The adhesive bond thus must retain its strength through the chemical etch and the hot solder dip, as well as in long-time actual service. The adhesive must have and retain electrical properties equivalent to those of the laminate base. It must not corrode the metal and should have no harmful residual solvents.

Bonding Ceramic Materials. The epoxy-resin adhesives which set at room temperature have found a number of interesting uses in the bonding and repairing of various ceramic materials. These adhesives are used as tie coats between old and new concrete in repairing highways, bridges, dams, and similar outdoor constructions. They are also used for bonding traffic markers to highways. Epoxy-resin adhesives have been found to be very useful in gluing pieces of decorative marble, which often cracks when thin slabs are sawed from blocks, without destroying the patterns. Similar epoxy adhesives are used for bonding marble and other stone windowsills in place and have recently been proposed for bonding concrete blocks in basement walls.

Tile Adhesives. Ceramic tile are now bonded to walls in large volume by using organic adhesives in place of the older inorganic mortar types. Adhesives include natural or reclaimed rubber bases in inorganic solvents, certain resin systems of unidentified chemical nature in solvents, and polymers or rubbers dispersed in water as emulsions or lattices.

Asphalt-base mastic adhesives, either as clay- or soap-stabilized emulsions or as cutbacks in hydrocarbon solvents, are widely used for bonding asphalt and vinyl-asbestos floor tile to wood or concrete subfloors in rapid on-the-job installations.

Similar mastic adhesives are used for bonding wood floor tile to subfloors. The cut-back types are used particularly where some water resistance may be needed, as on below-grade concrete slabs. Rubber tile and linoleum are bonded to subfloors either with low-moisture-resistant adhesives based on sulfite waste liquor concentrates or with more water-resistant types based on certain natural resins dispersed in alcohol. Very viscous mastics of rubber or asphalt bases are used for bonding acoustical tile to ceilings.

Adhesives for Shoe Manufacturing. A variety of quick-setting adhesives based on solvent dispersions of either rubber or cellulose nitrate are widely used in shoe manufacturing, particularly for women's shoes. In some applications the bond is intended as temporary until replaced by subsequent stitching or nailing. In other applications, as in some ladies shoes and sport shoes, the adhesive is the final fastening. Rubber-base adhesives are also widely used for bonding components in rubber footwear and for shoe repairing, particularly for attaching new soles and heels.

Assembly Adhesives. In addition to a number of previously cited examples, adhesives of various compositions are used for attaching and assembling a wide variety of items. Many of these are used in very small quantities per item, but total volumes in some cases may be quite sizable. Some of these uses include attachment of rubber-gasket linings around automobile doors and trunk lids and installation of sound-absorbing pads in automobile bodies. Similar adhesives are used in attaching various upholstery fabrics and trim in automobiles. These are large-volume uses and require low-cost adhesives, such as those based on reclaimed rubber in hydrocarbon solvents. These adhesives must develop a minimum level of holding power almost instantaneously as the bodies move down a production line. On the other hand, epoxy-type adhesives and even the high-cost ethyl cyanoacrylate adhesives, have been used in small quantities for assembly of jewelry items and special optical and electronic components. The growing interest in assembly of plastic model kits for hobbies has developed a sizable market for small-package, fast-setting adhesives. Solvent-type adhesives based on polystyrene or cellulose nitrate are most important in these operations. Industrial modifications of these adhesives are also used in factory fabrication of plastic toys and household items.

Evaluation of Adhesives

Because of the great variety of adhesives, adhesive applications, and bonded joints, the methods for evaluating adhesives are complex. Tests for structural adhesives are obviously more important and tend to be more elaborate and extensive than tests for holding or sealing adhesives. Generally, somewhat different methods of testing may be required for these varied adhesive applications, but many methods have certain similarities. The potential industrial user of a new adhesive in any critical bonding operation will usually be concerned with the potential strength that can be developed on the adherends in the proposed joints; the working or operating characteristics of the adhesive while in use; the stability in storage before use; and the permanence of the joints produced. Before he decides to use the adhesive, he will probably want a fairly extensive study of the properties in order to be certain that the adhesive and the bonding process are capable of meeting the important requirements. These studies are often known as qualification tests. It is often important to make less extensive check tests on different lots of adhesives to be certain that each meets a

certain minimum performance. These are often referred to as quality-control or inspection tests. Tests of actual production items may also be made to check the uniformity of the bonding process with a given adhesive over a period of time. Probably, the most complete listing of test methods of adhesives in the United States is that published by the American Society for Testing and Materials (ASTM). These methods include procedures for various strength tests, for working properties and for permanence. The ASTM compilation, which is revised at regular intervals, gives definitions of terms pertaining to adhesives as well as the test methods.

As previously noted, any strength tests of a bonded joint will depend both on the adhesive and on the bonding operation. With strength tests, particularly, it is therefore important to distinguish between tests of the adhesive itself as compared to tests of an adhesive-bonded product. In the first type the adhesive is used to fabricate a standard test specimen. Carefully selected and prepared adherends are used under controlled standard bonding conditions so that the resultant test values are a reliable indicator of the potentials of the adhesive itself. Tests on the bonded product from production are normally made on a standard type of test specimen. However, these are cut from an actual bonded item. Therefore, they may be of variable thickness and other variable dimensions and may be made up of different types or quality of adherends. They are then tested under the prescribed standard conditions. These test results are more a measure of the quality of the bonding operation, and often of the uniformity of the adherends, than an actual measure of the adhesive itself. Thus, in the case of adhesives for plywood, the adhesive is usually evaluated according to ASTM Method D 906, whereas the plywood is evaluated according to ASTM Method D 805, with both tests performed on the same type of shear-test specimen (26).

In strength tests, at least two distinct types of evaluation are of importance. First are the simpler test specimens and procedures that can be made rather rapidly and easily on readily available standard test machines and that give data which are primarily useful in the comparison of one adhesive with another under standard conditions. Such data may then be compared with similar data obtained at different times or even by different laboratories. An example of such a simple comparative test is the standard metal lap-shear test procedure described in ASTM D 1002 (26). It is readily recognized that these tests involve other types of stresses besides shear, and, thus, such data are not directly useful to design engineers. Therefore, a second type of strength test is needed to evaluate the adhesive in pure shear in order to satisfy the design engineer. Such a shear test, often proposed or used for this purpose, is a torsion test on metal tubes bonded end to end and loaded in torsion (27). Strains can be measured while under load, and stress-strain curves and various engineering calculations can be made. Such tests are essentially research studies that require much time and effort to make and test each specimen. The same distinction generally applies to tension, peel, fatigue, and other types of strength tests. Therefore, no single test procedure will satisfy both needs for information. Most of the published strength test procedures are intended for the simpler comparative tests. The more precise and fundamental test procedures have not yet been adequately developed or standardized and, therefore, are not usually included in present compilations of test procedures.

Initial strength tests of adhesives may include very simple knife, chisel, or pick tests by which bonds are crudely separated and the nature of the failure examined visually; more elaborate tension or shear tests in the case of rigid or semirigid adherends; or some sort of peel or pulldown tests where flexible adherends are con-

cerned. Other more extensive tests may include impact, cleavage, torsion, dead load, creep, and fatigue tests, all of which give different but useful information.

Some actual test values in the simpler types of strength tests may be of interest for illustration. It should be noted that often these strength values are not adequate indications of the full potential strength of the adhesive system used. In the case of many paper-bonding and wood-bonding adhesives, formulations are usually developed to be as strong as the paper or wood. That is, the joint is expected to fail always in the wood or the paper, and this is the usual criterion of a good joint for these adhesives. Thus, the actual failing load will depend on the strength of the adherend and such adhesives are formulated to provide only this level of strength.

In one study, block shear test specimens were prepared with several different species of wood using one urea-formaldehyde resin adhesive which cures at room temperature (28). The specimen and test procedures were as prescribed in ASTM Method D 905-49. Table 16 gives the shear test values obtained.

Table 16. Shear Test Values

Species of wood	Shear strength, psi
Sitka spruce	1,306
noble fir	1,632
sweetgum	1,769
yellow poplar	2,143
black walnut	2,393
yellow birch	2,840
hard maple	3,425

From the data one might infer that the adhesive was much stronger when used on yellow birch than on Sitka spruce. However, in all tests the specimens failed with estimated percentages of wood failure from 86 to 100, indicating that the strength of the wood was being tested rather than that of the glue. The shear strength of the particular adhesive was actually something greater than 3425 psi in these tests.

Various factors in the test procedure can influence test results. In the case of wood adhesives, these factors include the variability in wood pieces, moisture content, rate of load application, and variations in misalignment of specimens when under load. In one series of tests with the same block shear method (ASTM D 905-49) on hard maple but using several early polyvinyl acetate emulsion adhesives, shear test values as high as 4156 psi were observed (29). However, over 90 percent of the failure was in cohesion of the adhesive film. This unusually high shear value on maple, without failing the wood, was attributed to some relief of stresses during loading because of the partial plasticity of the glue line.

Structural metal-bonding adhesives, first developed extensively for use in military and naval aircraft, are usually evaluated by a simple lap-type shear test (ASTM D 1002-53T), using a specific aluminum alloy, 0.063 inch thick. Initial shear test values for a number of different types of such adhesives ranged from 1655 psi for a nitrile-phenolic adhesive to 4940 psi for a vinyl-phenolic adhesive. In most cases, failure was in cohesion of the adhesive film (30).

An extensive series of tests (31) of 10 typical structural metal-bonding adhesives on the same aluminum-to-aluminum lap-shear test specimen (ASTM D 1002-53T) gave initial shear values at 72 to 75°F of 2496 psi for a neoprene-phenolic-nylon adhesive

to 4561 psi for a vinyl-phenolic adhesive. Similar specimens tested at 178 to 182°F ranged from 934 psi for a neoprene-phenolic-nylon formulation to 4025 psi for a vinyl-phenolic adhesive. Similarly, when tested at -65 to -70°F, shear values were from 2414 psi for a neoprene-phenolic adhesive to 5090 psi for a neoprene-phenolic-nylon formulation. However, at higher temperatures, above 250°F, some of the other adhesives were much stronger than the vinyl-phenolic formulations.

In this same series of tests, similar aluminum lap specimens were subjected to axial fatigue at room temperature. The loads that could be tolerated without failure in 10 million cycles varied from 470 psi for a vinyl-phenolic adhesive to 1325 psi for a neoprene-phenolic adhesive. In some of the stronger specimens, the 0.063 inch aluminum alloy actually failed in fatigue in these tests.

Another important property of structural adhesives for aircraft is resistance to peeling. One of the most widely accepted tests for peel of aluminum-to-aluminum bonds is the climbing-drum test (32). In tests of 10 different structural adhesives with this procedure, average peel test values ranged from 6.3 inch-pounds (1 inch-pound = 0.113 joule, absolute) for a liquid epoxy-resin adhesive to 44.1 inch-pounds for a nitrile rubber-phenolic adhesive.

These limited strength test values for a few typical wood and metal-bonding adhesives serve mainly to indicate the complexity of the test data already in the literature and that being developed further at a fast pace. The data are nearly all for the comparative types of tests rather than for the research or fundamental types of evaluation. The data indicate that formulating an adhesive for a given use is generally a matter of compromise between various performance requirements. Very seldom does the same adhesive in a group have the highest test values in each of several types of strength tests. These principles apply to adhesives for many different purposes.

There is often a tendency to stress strength properties of adhesives at the expense of other properties such as convenience of use, adaptability to a particular type of simple or rapid-bonding technique, low cost, or high permanence. The strongest adhesive is often not the most suitable for the job. For example, many mastic adhesives, formulated of rubber or asphalt, which are widely used for bonding resilient or wood floor tiles to concrete subfloors may have shear strengths, measured by a modification of the block-shear test (ASTM D 905-49), of less than 50 psi, and yet they perform their assigned task entirely satisfactorily. Neoprene-base contact cements were developed largely for bonding high-density plastic laminates to wood-base counter or table tops. These adhesives develop a high degree of initial tack immediately after being assembled. They can then be rolled or tapped into place. The two adherends in this application are held entirely satisfactorily for long-time service. Yet, in the maple block-shear test (ASTM D 905-49) many of these adhesives have shear strengths of only 600 to 1000 psi.

Some adhesives for bonding flexible materials, such as fabrics or plastic films, are formulated to have plastic flow and to yield at rather low levels of strength in order to avoid excessive stress concentrations that might prematurely fail the adherends.

One important but largely unsatisfied need is reliable nondestructive test procedures for evaluating joint quality. Ideally, such a test should be sufficiently simple, rapid, and economical so that it could be used for screening every bonded product if the bond quality was considered critical. This type of test would then detect all bonds below a preselected standard of acceptance whether due to a substandard adhesive sample or to improper bonding conditions. Because of the great importance of

uniformly high quality bonds with structural metal-bonding adhesives for aircraft, considerable effort has been directed towards development and standardization of such nondestructive joint tests. Greatest emphasis has been on ultrasonic vibrations and instrumentation to detect responses from joints of different quality. Although considerable progress has been made and some industrial ultrasonic bond testers have been used in a few aircraft plants, it appears that at present such techniques are mainly suitable to detect a bond from a void. Their ability to distinguish a good bond from a mediocre or poor bond has not yet been adequately demonstrated.

Stability and working characteristics include storage life, viscosity or consistency, rate of spread, solids content, pH, flash point, and rate of strength development. The user may also require evaluation of such properties as degree of tackiness and tendency of one adhesive-coated surface to stick excessively to an adjacent one (blocking), or the detection by analytical methods of the presence of extenders, acids, or alkalies that are objectionable for certain uses. In some cases, it is necessary to make pilot runs on regular bonding equipment to determine the adequacy of the adhesive.

Because of the great strides in the development of synthetic-resin adhesives capable of long-time service under even severe service conditions, the need for adequate short-term tests of permanence is particularly great. A number of useful tests have been used to make crude comparisons of the relative permanence of different adhesives or of bonded joints. In order to give usable results within a few hours or days, the tests must involve rather severe treatments, such as boiling in water, steaming, heating, or exposure to heavy mold or other microbiological conditions. The adequacy of such tests can only be assessed by comparison with results of long-term controlled exposures or of actual service. Since service tests may require years before useful results are developed, the short-term tests must often be used before their validity can be fully established. One present obstacle to development of more adequate permanence tests is a general lack of real understanding of the fundamental mechanisms by which adhesive bonds actually deteriorate in service. When such mechanisms are more clearly understood, it will be relatively simple to accelerate these reactions for the short-term tests in which the user can place greater confidence. In spite of these limitations, the potential user or purchaser has on hand a variety of test procedures for various adhesive applications and more are being actively investigated each year.

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ADIPIC ACID

Adipic acid (hexanedioic acid, 1,4-butanedicarboxylic acid), $\text{HOOC}(\text{CH}_2)_4\text{COOH}$, is a white crystalline solid, molecular weight 146.14, melting point 152.1°C .

From a humble beginning as a natural constituent of sugar beets (1), adipic acid has established itself as a most important member of the well-known class of organic compounds, the dicarboxylic acids. In the course of a relatively few years, it has become widely used in the production of synthetic fibers, coatings, plastics, urethane foams, elastomers, and synthetic lubricants, all of which are among the fastest growing fields of modern technology. The discovery of nylon, a polyamide, by W. H. Carothers in the laboratories of the Du Pont Company in the early 1930s inaugurated a new era of synthetic textile fibers. It also stimulated the development of a commercial process for the production of adipic acid since the nylon synthesis was based on the use of this material. Accordingly, the first commercial production of adipic acid in the United States was begun by the Du Pont Company in 1937.

In the twenty-odd years that have elapsed since that time, the production of high-quality adipic acid has constantly grown. The largest portion of this material is consumed in the synthetic textile field. Nylon-6,6, which is the first and still most important type of nylon, is made by heating the salt of adipic acid and hexamethylene-

diamine. Because of their versatility, adipic acid and adipic acid derivatives are meeting the demands of an expanding technology for new materials with brand new properties and varied product characteristics. Because of consistently high quality and reliable sources of supply, adipic acid is used in foods, resins and plastics, coatings and finishes, foams and elastomers. (See Polyamides; Polyesters; Coatings; Foams; Elastomers.)

Physical Properties

Adipic acid is a white, crystalline, odorless solid with a slightly acid taste, and is characterized by the following typical data (2): density, real (solid), 1.366 g/cm³, apparent (crystals), 0.635 g/cm³ (39.6 lb/ft³); mp, 152.1°C; bp at 760 mm Hg, 330.5°C (with decomposition), at 100 mm Hg, 265.1°C, and at 10 mm Hg, 205.5°C; flash point (Cleveland open cup), 210°C; fire point (Cleveland open cup), 232°C; viscosity (of melt) at 160°C, 4.54 cps, and at 193°C, 2.64 cps. The pH values for water solutions of adipic acid at 25°C are as follows:

Adipic acid, wt %	0.1	0.2	0.4	0.6	1.2	2.5
pH	3.2	3.1	3.0	2.9	2.8	2.7

Adipic acid is a dibasic acid ionizing in two steps: k_1 at 18°C, 4.6×10^{-5} , at 25°C, 3.6×10^{-5} ; k_2 at 18°C, 3.6×10^{-6} , at 25°C, 2.9×10^{-6} . It is monoclinic, forms needles, and has the following refractive indexes (5461 Å): α , 1.488 ± 0.002 ; β , 1.505 ± 0.005 ; and γ , 1.593 ± 0.002 . Birefringence, 0.105, and optical axial angle: 2Ha, $74^\circ \pm 1^\circ$; 2V, 74° ; and 2Ho, $105^\circ \pm 1^\circ$. It is nonhygroscopic at 27°C and 85% relative humidity. Heat of combustion, 668.6 kcal/g-mole; heat of fusion, 4.0 kcal/g-mole; heat of vaporization, 19.120 kcal/g-mole; heat of sublimation, 23.120 kcal/g-mole; heat of solution (water) at 10–20°C, -7.460 kcal/mole, and at 90–100°C, -15.800 kcal/mole; specific heat of solid, 0.583 cal/g; and specific heat of vapor (estimated), 0.402 cal/g at 300°C.

Adipic acid is slightly soluble in water and very soluble in methanol. The temperature-solubility characteristics in various solvents are shown in Figure 1. The solubility of adipic acid can be increased appreciably by using binary mixtures of water with methanol, ethanol, or acetone (3). Table 1 gives solubilities in mixtures of water with acetone and ethanol.

Table 1. Solubility of Adipic Acid in Binary Mixtures at 40°C

Weight percent of solvent in water	Grams of adipic acid per 100 grams of mixture	
	Acetone	Ethanol
0	5.2	5.2
20	15.0	13.7
40	28.2	25.9
60	35.9	34.0
80	32.4	33.5
100	8.7	22.4

Toxicity studies carried out in cooperation with the U.S. Food and Drug Administration, including several years of animal feeding, metabolism, and pathological testing

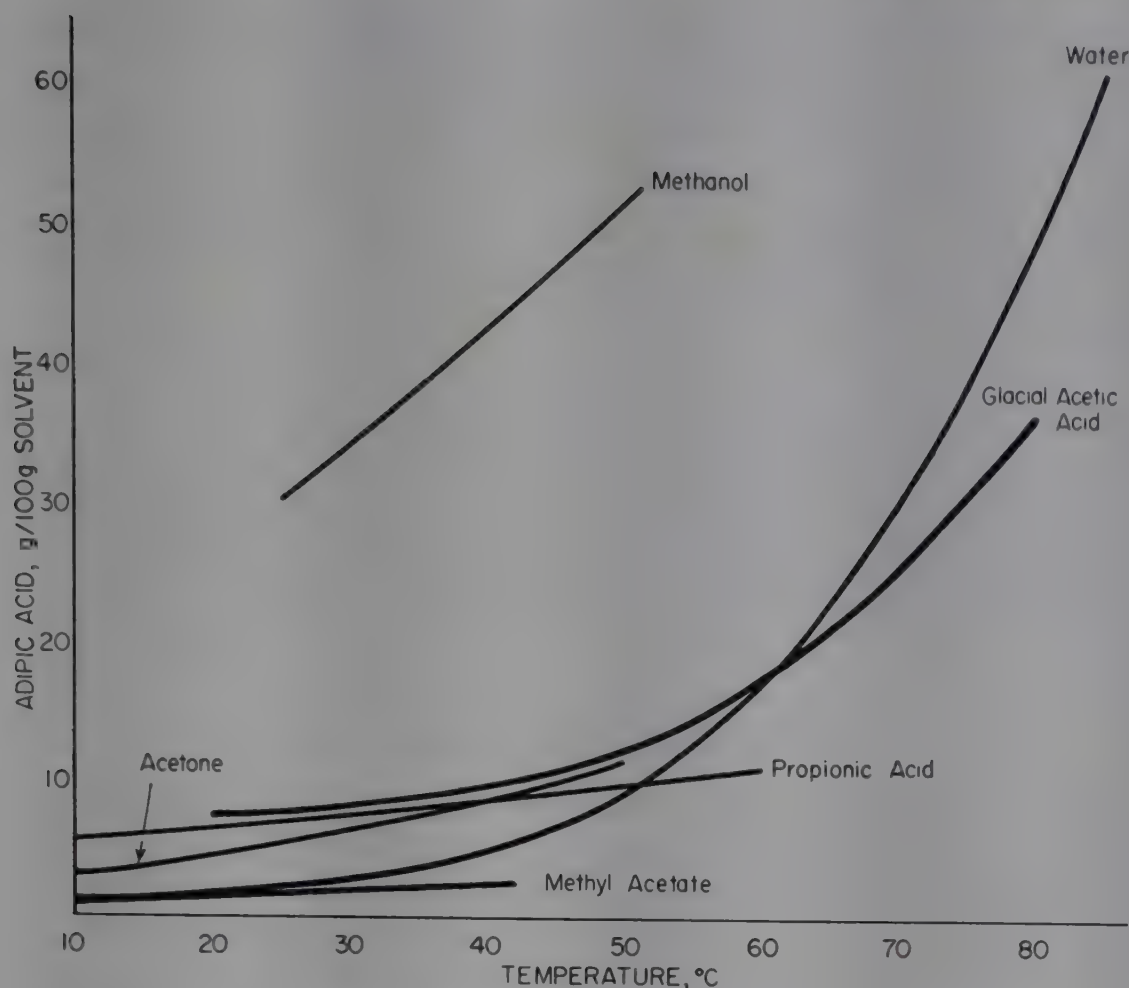


Fig. 1. Solubility of adipic acid.

(4) provide a firm basis for the acceptance of adipic acid as a component for non-standardized foods (5). No hazards are encountered through the handling of adipic acid in the usual applications.

Chemical Properties

Stability. Adipic acid is relatively thermally stable under a nitrogen blanket; heating for 15 hours at 232°C is required to develop a marked discoloration. Accompanying the decomposition, significant amounts of water, carbon dioxide, and cyclopentanone, and some valeric acid, C_4H_9COOH , are formed. At 300°C decomposition to cyclopentanone is nearly quantitative (6). The presence of compounds such as calcium oxide (7,8) and basic barium salts (9) markedly accelerates the reaction. Cyclopentanone can be conveniently prepared by heating a mixture of barium hydroxide and adipic acid at 285–295°C; yields of 75–85% are obtained. Holding adipic acid for four minutes at its boiling point results in the formation of as much as 7% of polymeric adipic anhydride (10). (See p. 408.) The mechanism of the thermal decomposition of adipic acid and its esters is believed to involve the formation of cyclopentanone-2-carboxylic acid (or its ester) as the first step, followed by decarboxylation (6).

Adipic acid is particularly stable toward oxidation; in fact, a good method of purifying the acid is by recrystallization from nitric acid. Under manufacturing conditions, there is very little attack on adipic acid by air oxidation, even though it is heated under pressure to temperatures as high as 275°F (11,12). Under mild conditions with hydrogen peroxide in the presence of cupric salt at 60°C, adipic acid is oxidized to carbon dioxide, and volatile carboxylic acids including formic acid and

succinic acid ($\text{HOOC}(\text{CH}_2)_2\text{COOH}$) (13). These products indicate random attacks of the hydrocarbon chain in both the alpha and beta positions.

Under somewhat more vigorous conditions, adipic acid has been oxidized with chromic acid to give carbon dioxide, water, and succinic acid as the only isolable products (14). Other oxidizing agents, such as potassium permanganate, attack the acid even at room temperature, but the reaction is very slow. The only oxidation products which seem to have been isolated in this reaction are carbon dioxide and water.

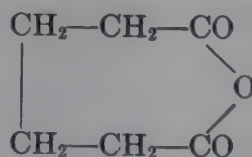
Maleic anhydride has been identified as the reaction product of cyclohexane and air over vanadium pentoxide at the vapor phase at 400°C (15). Under mild conditions, vanadium pentoxide in sulfuric acid, dilute permanganate, ceric sulfate, hydrogen peroxide, sodium hypochlorite, periodic acid, or peracetic acid appear to have little effect on adipic acid, although each of these reacts with the acid under more vigorous conditions.

Chemical Reactions

Adipic is a dicarboxylic acid and undergoes reactions typical of carboxylic acids, including salt formation, amidation, esterification, acid halide formation, halogenation, and others. Some of these reactions lead to products of commercial importance.

Salt Formation. Adipic acid reacts with basic materials to give both acid and neutral salts. In the case of the rare earth elements, it forms insoluble simple salts with members of the cerium group (La, Ce, Pr, Nd, and Sm) and soluble complexes with those of the yttrium group (that is, those rare earth metals that are not precipitated by ferrocyanide, namely Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y) (16). Adipic acid forms salts with the polymethylenediamines which have characteristic melting points (17,18). The diamine salts are easily prepared by bringing together alcoholic solutions of equivalent amounts of the reactants. The salts of ethylenediamine and hexamethylenediamine have been reported in the literature (19).

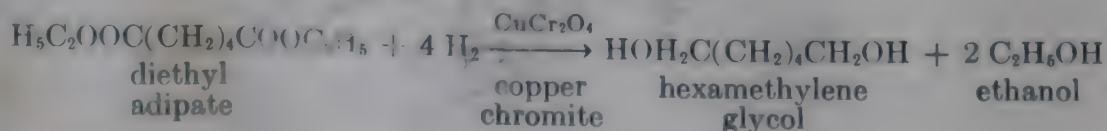
Anhydride Formation. Adipic acid produces a polymeric anhydride, $(-\text{OCOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}-)_n$, when heated with acetyl chloride or acetic anhydride (20). Similar polymers are obtained with higher homologs of the dicarboxylic acid series. The cyclic monomeric form of adipic anhydride,



a liquid freezing at 20°C , can be prepared by distilling the polymeric form in a vacuum. Adipic anhydride is unstable and will repolymerize quite readily (18).

Acid Chloride Formation. Adipoyl chloride may be prepared from adipic acid with sulfurous oxychloride (21), zinc chloride and phosphorus trichloride (22), or phosphorus pentachloride (23). It boils at 125°C at 11 mm and $83-85^\circ\text{C}$ at 1-2 mm.

Reduction. The catalytic reduction of diethyl adipate with hydrogen over a copper chromite catalyst at 225°C , at 2000-3000 psi, forms hexamethylene glycol in high yield (24).

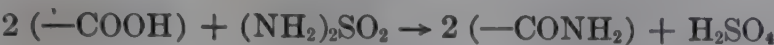


Diethyl adipate can be reduced noncatalytically by reducing agents such as lithium aluminum hydride in ether at room temperature (25).

Amidation. Adipamide is easily prepared by heating adipic acid in the presence of ammonia (26,27). It also may be prepared from the acid by reaction with formamide (28),



or sulfamide (29),



N,N'-Dialkyl- and *N,N,N',N'*-tetraalkyladipamides are made by reacting primary and secondary amines, respectively, with adipic acid heated in the presence of zinc chloride (30), or with adipamide (31), or with adipic esters such as diethyl adipate (32,33), or with adipoyl chloride (33).

N,N'-Dibenzyladipamide has been prepared by the addition of adipoyl chloride to silver dibenzyl phosphate in ethanol to give adipoyl bis(dibenzyl phosphate) which is treated with benzylamine in a borate buffer at pH 7.4 in dioxane (34). *N,N'*-Diphenyladipamide was prepared in a similar manner. *N,N'*-Dibromo- or *N,N'*-di-

Table 2. Melting Points, Boiling Points, Densities, and Refractive Indexes of Adipic Acid Esters

Ester	Melting point, °C	Boiling point, °C/mm	Density, d ₄ ²⁰	Refractive index, n _D ²⁰
monomethyl adipate	3	160/12		
monoethyl adipate	28–9	169–170/17	1.081	1.4384
monopropyl adipate		146/4	1.0574	1.4401
monobutyl adipate		155.5/4	1.0377	1.4418
dimethyl adipate	8.5	110/12	1.0625	1.4284
diethyl adipate	–21.4	127/13	1.0261	1.4272
dipropyl adipate	–20.3	155/10	0.9790	1.4314
diisopropyl adipate		136/14		
dibutyl adipate	–37.5	145/4	0.9652	1.4369
diisobutyl adipate			0.957	1.428 ^a
di- <i>sec</i> -butyl adipate		153–154/10	0.9543	1.4301
di- <i>tert</i> -butyl adipate	10	116/1.5		
diamyl adipate (mixture <i>n</i> - and iso-)	–14			
diisoamyl adipate (di(3-methylbutyl) adipate)		190/15	0.9455	1.4343
di- <i>n</i> -hexyl adipate	–8		0.933 ^b	1.439 ^a
di(1,3-dimethylbutyl) adipate			0.926	1.433 ^a
dioctyl adipate	9.7	175/2	0.9135	1.4402 ^a
diisooctyl adipate (mixed isomers)			0.928	1.448 ^a
dicapryl adipate			0.915	1.440 ^a
di(2-ethylhexyl) adipate			0.927	1.447
dinonyl adipate	21.6		0.914 ^b	1.445 ^a
di(3,5,5-trimethylhexyl) adipate	–10	206/5	0.9130 ^b	1.4455 ^a
di- <i>n</i> -decyl adipate	26	244/5	0.896	1.4481 ^a
ditridecyl adipate	45.9		0.891	1.459 ^a
dicyclohexyl adipate	36–8	212/12	1.013 ^c	1.4702 ^a
di(2-methoxyethyl) adipate		185–190/11	1.075 ^b	1.439 ^a
bis(2-methoxymethoxyethyl) adipate		199/2.5	1.112 ^d	1.4402 ^a
di(2-ethoxyethyl) adipate		165/4	1.036 ^b	1.439 ^a

^a n_D²⁵

^b d₄²⁵

^c d₄²⁵

^d d₁₅^{15.5}

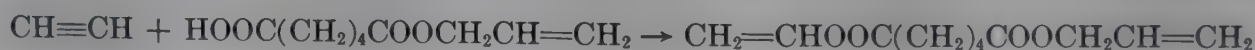
chloroadipamide has been prepared by the interaction of adipamide and bromine or chlorine in the presence of sodium bicarbonate (35). Cyclic adipamides such as ethyleneadipamide and dimeric ethyleneadipamide (36) have also been described.

Esterification. Esterification is one of the important chemical reactions of adipic acid. The mono- and diesters of this acid are easily prepared by direct esterification with the alcohol in the presence of an acid catalyst. Diesters of the higher-molecular-weight alcohols are also readily prepared in nearly quantitative yields by transesterification with dimethyl or diethyl adipate. This latter method is best suited when an acidic catalyst cannot be used, as when the alcohol component contains structures attacked by acid. Monoesters are prepared by heating a mixture of adipic acid and the diester. The melting points, boiling points, densities, and refractive indexes of some of the esters are listed in Table 2.

Mixed esters of adipic acid, such as methyl butyl adipate, may be obtained by first forming the monoester of one alcohol and then reacting this acid ester with a second alcohol. Other complex esters can be obtained—for example, by reacting one mole of adipic acid with two moles of a dihydric alcohol and then with two moles of a monobasic acid. An example of this type is di(2-propionyxyethyl) adipate, $(-\text{CH}_2-\text{CH}_2\text{COOC}_2\text{H}_4\text{OOC}_2\text{H}_5)_2$. Another type of complex ester, such as $(-\text{CH}_2\text{OOC}_4\text{H}_9-\text{COOC}_4\text{H}_9)_2$, is obtained by the reaction of two moles of adipic acid with one mole of dihydric alcohol and then with two moles of a monohydric alcohol.

Other methods of preparing esters of adipic acid include reacting adipoyl chloride with alcohols (37), treating polymeric adipic anhydride with alcohol (38), and reacting disodium adipate with an alkyl halide (39). Phenolic esters such as diphenyl adipate are prepared by the direct esterification procedure in the presence of trifluoroacetic anhydride (40).

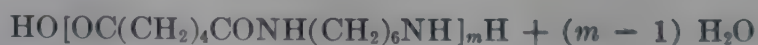
Mixed unsaturated esters of adipic acid have been prepared by reacting the monoester of an unsaturated alcohol containing at least three carbon atoms with acetylene in the presence of a catalyst. In this manner, vinyl allyl adipate was obtained (41).



CONDENSATION POLYMERIZATION

Adipic acid is a bifunctional acid and, therefore, can enter into condensation polymerization reactions with other bifunctional compounds such as diamines, glycols, and amine alcohols.

Polyamides. The most important of these condensation reactions is the polycondensation of adipic acid with diamines to give polyamides or nylons (42). This reaction with hexamethylenediamine may be represented as follows:



The polyamides of adipic acid are thermoplastic resins melting above 200°C. The one obtained with hexamethylenediamine (nylon-6,6) melts at 250°C.

Polyesters. Another important polymerization reaction of adipic acid is polycondensation with the glycols to form polyesters (43). Polymerization with ethylene glycol may be represented as follows:



The polyesters of adipic acid are solids with melting points ranging from 50°C for poly(ethylene adipate) to 77°C for poly(decamethylene adipate) (43). Adipic acid may be used in combination with unsaturated or other saturated dicarboxylic acids for polycondensing with polyhydric alcohols to form polyesters—for example, the preparation of modified maleic or phthalic alkyd resins to impart flexibility to the final crosslinked composition.

Polyester Amides. Adipic acid is polycondensed with monoaminomonohydric alcohols to form polyester amides (44). The reaction with monoethanolamine may be represented as follows:



Polyester amides may be synthesized from adipic acid and mixtures of diamines and polyhydric alcohols (45), or with mixtures of monoaminomonohydric alcohols and polyhydric alcohols.

Manufacture

Information on the manufacture of adipic acid has appeared many times in the literature, and this discussion is based entirely on such published data. (Two of the best references are 11 and 12.)

Adipic acid is manufactured commercially from one of two basic raw materials, either phenol or cyclohexane. Cyclohexane may be converted by air oxidation to a mixture of cyclohexanol and cyclohexanone. Phenol may be hydrogenated to cyclohexanol. The alcohol-ketone mixture, or the alcohol alone, may then be oxidized to adipic acid using nitric acid. Figure 2 illustrates the process schematically.

Since a high degree of purity is required for the production of nylon-6,6, as well as

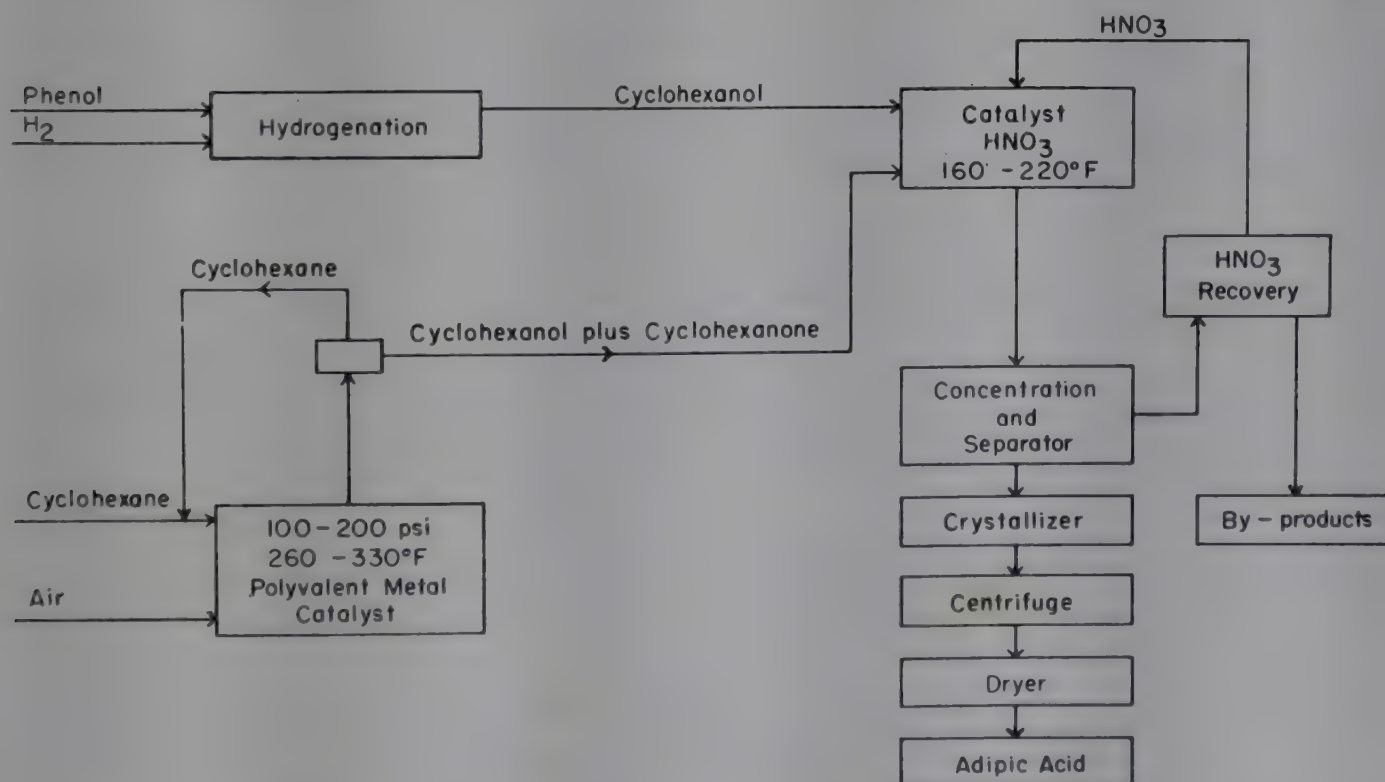


Fig. 2. The manufacture of adipic acid from either phenol or cyclohexane. The hydrogenation can be accomplished under a variety of conditions that depend on the catalyst, hydrogen purity, and reactor cooling methods.

for other end uses, the crude adipic removed from the reaction products is usually dissolved in water and recrystallized, followed by drying.

Other less efficient routes have been explored, including single-step nitric acid oxidation of cyclohexane, an air-potassium permanganate reaction, and the use of liquid nitrogen dioxide. These processes are described in the patents listed in the Processes and patents section of the bibliography.

ECONOMICS (46)

With the growth of the synthetic fiber industry, the importance of adipic acid as a chemical intermediate has grown rapidly. Du Pont, the first producer of adipic acid in the United States, continues as a leader in the production of adipic acid for their fiber production, and, in consumer sales, for food products, ester-lubes, plasticizers, and polyurethane elastomers, coatings, fibers, and foams. Other adipic acid producers are Monsanto Chemical Company, Allied Chemical Corporation, and Chemstrand Corporation.

Plant locations and estimated productions, as given in the *Oil, Paint and Drug Reporter* of December 25, 1961, are as follows:

Producer	Location	Estimated capacity, million lb/yr
Chemstrand	Pensacola, Fla.	over 200
Du Pont	Belle, W. Va., and Orange, Tex.	200
Allied Chemical	Hopewell, Va.	20
Monsanto Chemicals	Luling, La.	20
	Total	over 440

Requirements for uses other than nylon (47), although growing rapidly—sales equaled 40 million pounds in 1960—still represent less than 10% of the total U.S. production capacity. Nylon-6,6, a copolymer of adipic acid and hexamethylenedi-amine, continues to be by far the most significant factor in the economic future of

Table 3. Carload Quantities, Delivery in Bags (fob)

Year	Price, \$/lb		Sales, million lb
	High	Low	
1961	0.3225	0.290	
1960	0.3225	0.3225	40,320
1959	0.3225	0.3225	34,105
1958	0.3225	0.3225	
1957	0.3225	0.3200	

adipic acid. Competition from other synthetic fibers may be expected but, because of the excellent properties and firm position in many use areas, nylon-6,6 should show continued growth.

The price of adipic acid for consumer sales for the period 1957–1961 is shown in Table 3 (48,49).

SPECIFICATIONS

The commercial product is a white crystalline, odorless, free-flowing solid which analyzes 99.8% adipic acid. It is one of the purest chemicals being manufactured on a large scale. A typical analysis for the product manufactured by E. I. du Pont de Nemours & Co., Inc., is as follows:

adipic acid, %	99.8
melting point, °C	151.9
water, %	0.06
ash, ppm	5.4
iron, ppm	0.5
color, APHA (20 g in 100 ml methanol)	1.2

Methods for Determining Purity. The determination of the exact purity of commercial adipic acid is complicated by the low level of impurities present. Depression of melting point cannot be used as a criterion of purity. The low level of impurities present, such as succinic acid, does not affect the melting point sufficiently to be detected by the most sensitive instrument. Similarly, small quantities of closely associated dibasic acids have little effect on the theoretical neutralization equivalent of 73.07 for adipic acid.

An accurate and precise method for determining the purity of adipic acid is found in a freezing point depression determination. The apparent freezing point of adipic acid can be measured with greater precision than the melting point, because it is less dependent on the rate of heat transfer and, in general, equilibrium is more closely approached. The method consists of carefully melting a quantity of adipic acid in a cryoscopic tube under controlled conditions and measuring the apparent freezing point with a Mumberg thermometer, platinum resistance thermometer, or thermistor. Inasmuch as adipic acid decomposes very slowly at temperatures in the region of its melting point, which prevents the measurement of its true freezing point, the freezing point depression is obtained by taking the difference between the freezing points of the sample and of a primary standard. The freezing point depression can be obtained with a precision of $\pm 0.007^{\circ}\text{C}$ standard deviation, which corresponds to about 0.014% by weight calculated as succinic acid.

Water in the amounts present in the product has a major effect on the apparent freezing point. Because the proportion of water lost during melting varies slightly with the initial concentration, an empirical correction is applied to permit the comparison of apparent freezing points on an anhydrous basis. To determine water concentration with the precision required for this correction, an improved Karl Fisher technique is used which permits water to be determined with an accuracy of $\pm 0.001\%$ standard deviation.

If traces of low-molecular-weight monobasic acids are in the commercial product, they can be determined by a two-plate steam distillation of a weighed sample. The distillate is collected in equal portions and titrated with 0.01N sodium hydroxide using phenolphthalein as the indicator. The procedure has a precision of ± 2 moles per million of monobasic acid.

Methods of Purification. Adipic acid is readily purified by recrystallization from acetic or nitric acid, followed by recrystallization from water. Another method consists of extracting an aqueous solution of adipic acid with chloroform using a Scheibel countercurrent extraction column, followed by steam distillation and recrystallization.

An ash-free acid may be prepared by hydrolysis of a purified ester or by vacuum distillation of the free adipic acid, followed by recrystallization from conductivity water.

Analytical Methods for Identification. The presence of adipic acid in a material is readily determined by identification of one or more of its derivatives, which are easily prepared by standard procedures. The most common derivatives of adipic acid are as follows:

<i>Derivative</i>	<i>Melting point, °C (50)</i>
amide	220
anilide	240
<i>p</i> -toluidide	241
<i>p</i> -nitrobenzyl ester	105
<i>p</i> -bromophenacyl ester	154
<i>p</i> -phenylphenacyl ester	148

The adipic acid content of a material may be precisely determined by a number of methods. If it is the only acid present, as might be the case in a powdered gelatin dessert, electrometric titration with sodium hydroxide is a satisfactory procedure. When other acids or interfering compounds are present, a method utilizing isotope dilution of the sample with radio-labeled (carbon-14) adipic acid may be used. After addition of a known amount of labeled acid to the sample in solution, adipic acid is recovered from the solution by crystallization and is purified. Because the labeled acid has the same solubility behavior as the normal acid, the measured radioactivity of the recovered material then indicates the extent to which the added acid has become diluted with normal acid and, hence, the percentage of adipic acid in the original sample. This method is considered to be absolute. Other methods that have been successfully employed include partition chromatography with a silicic acid column (51-53) and infrared absorption of the sodium salt.

Uses for Adipic Acid and Its Derivatives

The principal use of adipic acid is in the preparation of derivatives; however, the nonhygroscopic, mildly acidic, and nontoxic properties enable the acid to find use in a number of applications. In the food industry the acid is used along with citric and tartaric acids, and potassium bitartrate. Anhydrous adipic acid shows no weight gain on exposure for six days at 80°F and 85% rh, whereas anhydrous citric acid gains 5.7% under the same exposure. This property lessens caking and improves storage stability of dry formulations where it also contributes a clean, tart taste and pH control.

It is used for its flavor and acidity in gelled desserts (54,55) and pudding mixes (56,57), fruit-flavored beverages (58), jams and jellies, candies, and flavoring extracts. Other areas that utilize this mild acidity are cosmetics, water treatment, metal finishing, and dairy industry.

Salts. Sodium adipate, as a masking agent in the chrome tanning of leather (59), eliminates pickling and basicity adjustment. It provides quicker tannage and economy in use of the chrome liquor, producing a firmer leather of higher chromium content. It also is used as a lubricant for polymers and copolymers of vinyl acetate, which permits use of higher drying temperatures, resulting in better flow and storage properties (60). Monopotassium adipate has been applied in the dyeing of leather to make the coloration of acid or substantive dyes more level and resistant to soaps and

alkalies (61). Ammonium adipate is useful in the printing of textiles for restoring, locally, the luster of cellulose acetate (62). This process is an improvement on thiodiglycol which tends to cause outlines to spread during steaming. Ammonium adipate is also used in the color printing of textiles, in finishing in conjunction with starch and formaldehyde, and in the treatment of calico fabrics, pile fabrics, linen, shirtings, collars, and animal fibers (63). The triethanolamine salt is of interest in adhering glass to glass or metal (64). The diphenylmercury and dixylylmercury adipates have been patented as antiseptic and germicidal compounds (65).

Anhydrides. Polymeric adipic anhydride hardens polyvinyl chloride compositions (66). Cyclic adipic anhydride is a crosslinking agent for polyester amides (67). It converts soft, waxlike polyester amides into solvent-resistant, elastic, pliable materials.

Acid Chloride. Tough, waxy, water-soluble polyoxyethylene glycol esters are produced by treating polyoxyethylene glycols of high molecular weight with adipoyl chloride (68). These are useful for producing destructible wax patterns for precision casting molds. Linear polythioesters suitable for molding or drawing into a fiber may be prepared by the interaction of dimercaptans and adipoyl chloride (69). Quaternary ammonium compounds useful as water-repellent or softening agents for textiles are prepared by combining a tertiary aliphatic or heterocyclic amine in the presence of a catalyst with the reaction product of adipoyl chloride, formaldehyde, and an aliphatic nitrile with more than seven carbon atoms (70). Condensation products of adipoyl chloride with mineral oil have been patented as pour-point depressants for waxy mineral oils (71). Esterification of cellulose acetate with adipoyl chloride lowers the swelling capacity and solubility of cellulose acetate in acetone, chloroform, and glacial acetic acid (72). 5-(2-Thienoyl)valeric acid is prepared from adipoyl chloride and thiophene in the presence of a silica-alumina or 85% phosphoric acid catalyst (73), and is useful as an intermediate in the manufacture of plastics, pharmaceuticals, and dyes.

Adipamide and Its N,N' -Substituted Derivatives. Adipamide can be used in the preparation of adiponitrile which may be hydrogenated to hexamethylenediamine, a component of nylon-6,6 (74). N,N' -Dioctadecyladipamide is a foam inhibitor in steam boilers (75). N,N' -Didecyladipamide is useful as a gelling agent for coating vehicles and hydrocarbon solvents (76). N,N,N',N' -Tetramethyladipamide is a solvent for vinylidene chloride polymers (77). Hair can be permanently waved by treatment with N,N' -bis(acetylthiomethyl)adipamide (78). The sodium salt of sulfonated N,N' -bis(2-hydroxyethyl)adipamide is useful as an anionic detergent (79). The N,N' -dibromo- and N,N' -dichloroadipamides have been applied to the crosslinking of cellulose fibers (35). The unsaturated ester amide, N,N' -bis(2-carballyloxyethyl)adipamide, which is prepared by reacting N,N' -bis(2-hydroxyethyl)adipamide with allyl chloroformate, can be polymerized in the presence of heat, light, or catalysts such as peroxides. The polymers are useful in coating compositions, laminated fabrics, cloth impregnation, and adhesives (79).

Esters. The higher esters of adipic acid are effective plasticizers for many polymeric materials including polyvinyl chloride and its copolymers (80–82), natural and synthetic rubbers (83, 84), polystyrene (85), and cellulose derivatives (81). These esters are easily incorporated into the polymer by the usual methods. They have a high degree of compatibility and impart exceptionally good low-temperature properties. Compatibilities of a number of typical adipates with polyvinyl chloride, polystyrene, ethyl cellulose, cellulose acetate, and nitrocellulose are given in Table 4.

Table 4. Compatibility of Adipate Esters with Various Resins^a

Plasticizer	Polyvinyl chloride ^b	Poly-styrene ^c	Ethyl cellulose ^d	Cellulose acetate ^e	Nitro-cellulose ^f
di- <i>n</i> -decyl adipate	C ^g	C	C	I	C
di(2-ethylhexyl) adipate	C				
di(3,5,5-trimethylhexyl) adipate	C ^g	C	C	I	C
di- <i>n</i> -butyl adipate	C	I	C	C	C
dicyclohexyl adipate	C	C	C	I	C

^a C and I denote compatibility and incompatibility, respectively, for ester content indicated.

^b Blended by milling composition containing 33.3% plasticizer.

^c Blended by casting films from 20% polymer benzene solution containing 9.1% plasticizer and 90.9% polystyrene.

^d Blended by casting films with 15% solution of ethyl cellulose in 80:20 toluene-ethanol. Films contain 13% plasticizer and 87% ethyl cellulose.

^e Blended by casting films from 20% polymer acetone solution containing 20% plasticizer and 80% cellulose acetate.

^f Blended by casting films from 20% polymer butyl acetate solution containing 16.7% plasticizer and 83.3% nitrocellulose.

^g Exuded slightly.

An outstanding feature of the adipate esters (86) in polyvinyl chloride is their excellent low-temperature performance. The brittleness temperatures for compositions containing most adipates are between -41°C and -54°C . These values are much lower than for polyvinyl chloride plasticized with di(2-ethylhexyl) phthalate (DOP) and very much lower than for the tricresyl phosphate (TCP), which are other commercially important plasticizers. The excellent low brittleness temperatures imparted by the adipates are maintained in blends with other plasticizers; for example, plasticized polyvinyl chloride containing 33.3% of a 50:50 blend of di-*n*-decyl adipate and DOP has a low brittleness temperature of -48°C as compared with -28°C for DOP. The adipates give tensile strengths and ultimate elongations comparable to DOP. Compositions containing di-*n*-decyl adipate or di(3,5,5-trimethylhexyl) adipate are somewhat stiffer at 25°C than those containing DOP, but the adipates are more flexible at low temperatures, even in blends with other plasticizers.

Di-*n*-decyl adipate and di(3,5,5-trimethylhexyl) adipate tend to exude from polyvinyl chloride, but not in adipate-phthalate blends. Blending of the adipates of 3,5,5-trimethylhexanol and cyclohexanol almost eliminates exudation; the use of a mixed adipate ester of these two alcohols eliminates this deficiency.

The heat-ageing performance of various adipate esters is determined by weight loss and stiffness correlated with their respective volatilities.

Plastisols prepared with di-*n*-decyl adipate or di(3,5,5-trimethylhexyl) adipate and blends of other plasticizers have low initial viscosities and low rates of viscosity increase.

Adipates of numerous branched-chain alcohols and monohydric ether alcohols have found use as synthetic lubricants. Some of these are diisoamyl adipate (87), di(2-ethoxyethyl) adipate (88), di(2-ethylhexyl) adipate (89), and di(3,5,5-trimethylhexyl) adipate (90). These esters are particularly useful for operations at very low temperatures. They combine a very high viscosity with a very low pour point. For example, di(3,5,5-trimethylhexyl) adipate has a viscosity index of 161 and a pour point below -70°C (91). Adipate esters are added to other synthetic ester lubricants

to increase viscosity of the base fluid and to improve the viscosity-temperature characteristics (92).

Hydraulic fluids of good temperature stability and lubricating properties are prepared from the diadipates of ethylene glycol or diethylene glycol in a solvent such as isobutyl alcohol (93). These fluids are reported to cause virtually no swelling of rubber parts, have viscosities which are nearly independent of temperature, and are noncorrosive to ferrous and nonferrous metals.

Unusual applications for adipates include insect repellents (94), DDT emulsions (95), and emulsifying agents (96).

Diallyl adipate (97), divinyl adipate (41), and allyl vinyl adipate (98) can be polymerized in the presence of a catalyst such as benzoyl peroxide to give transparent resins. These unsaturated esters have been copolymerized with unsaturated esters of monocarboxylic acids such as vinyl acetate to give similar resins (99). Monoesters of adipic acid are used to dissipate static charges from resins such as vinylidene chloride (100). Monoesters improve drying velocity and luster of lacquers (101). Monoethyl adipate inhibits foam in automotive lubricating oils (102). Monoesters are catalysts for urea- and/or thiourea-formaldehyde molding powders (103). 2-Methyl-1,4-monoadipyl-naphthohydroquinone from adipic anhydride and 2-methyl-1,4-naphthohydroquinone is reported as having the antihemorrhagic action of vitamin K (104).

Polyamides. Polyamides made from adipic acid and hexamethylenediamine (nylon-6,6) are the predominating single type. Nylon-6,6, the first purely synthetic textile fiber, possesses toughness; high tensile, impact, and flexural strength; and high resistance to chemicals, greases, and solvents other than mineral acids. It is resistant to boiling as well as freezing temperatures (105). Nylon-6,6 and other nylons are available as molding powders, filaments, sheets, rods, and tubes. Finished products are made by injection and compression molding and extrusion. The list of actual and suggested articles of manufacture from nylon is long, and includes the following: hosiery, textile fibers, duck, carpets, sewing thread, coated fabrics, high-tenacity tire cord, fishing lines, racket strings, surgical sutures, paintbrush bristles, screening, rope, shock-absorbing tow line, photographic film base, sound records, shoe soles, insulated wire, bonded cork compositions, tubing, three-dimensional drawn objects, machine parts such as bearings and gears, bearing structures, sponge, lubricating-oil modifier, and armored vests. Solutions of nylon are also available. These are being used for casting into film, such as a photograph film base, and as insulating enamel for wire. Nylon wire enamel is tough and extremely resistant to abrasion, chemicals, and solvents.

Polyesters. The most important industrial application for polyesters of adipic acid is in the manufacture of polyurethane elastomers utilizing diisocyanate (106,107). The polyesters are prepared from ethylene glycol, diethylene glycol, 1,4-butanediol, propylene glycol, and blends of these and other glycols. The diisocyanates utilized are toluenediisocyanate, 1,5-naphthalenediisocyanate, and others. These elastomers have high gum tensile strength, high modulus, good resilience, excellent ozone resistance and ageing characteristics, low permeability, very high abrasion resistance, and high resistance to nonpolar solvents. Typical uses are in gaskets, hosing and tubing which are in contact with gasolines, spandex fibers, adhesives, varnishes, lacquers, coatings for paper and cloth, and mechanical goods requiring extreme toughness and high abrasion resistance, such as solid tires. Similar diisocyanate-modified polyesters

made with adipic acid, maleic anhydride, and glycols can be cured with benzoyl peroxide to give rubberlike materials (108).

Polyurethane flexible foams result from a diisocyanate and a polyester prepared from adipic acid, a glycol, and a trihydric alcohol, the latter comprising about 4% of the total polyester by weight. The reaction mixture is foamed by employing excess diisocyanate and water (which react to form carbon dioxide and a diamine). Numerous recipes are known which are based on a particular catalyst system and surfactant (foam stabilizer). The polyester-based foams are particularly useful where solvent resistance and cell characteristics are important.

Adipic acid polyesters are nonvolatile glycol plasticizers for polymeric substances such as alkyd resins (109), lacquers (110), and polyvinyl chloride resins (16,111). The polyester from adipic acid and trimethylolpropane polyester can replace linseed oil in making linoleum (107).

Synthetic lubricants are prepared by reacting adipic acid with glycols and small amounts of monocarboxylic acids or monohydroxy alcohols as terminating agents (112,113). Polyurethane adhesives have been prepared from adipate polyesters that contain unreacted hydroxyl groups but no free carboxylic acid groups (114). Mixed polyesters of adipic acid and phthalic acid with glycerol or pentaerythritol copolymerized with diisocyanate are used as adhesives in the shoe industry (115).

Polyester Amides. Synthetic polyurethane elastomers are made from polyester amides of adipic acid (107,116). These polyester-amide elastomers are reported to be tough, durable, and solvent resistant. Similar synthetic elastomers may be made by crosslinking with adipic anhydride (67).

Elastomeric polyester amides of adipic acid are also prepared by extending the polymeric chain with an organic diisocyanate and crosslinking the extended chain with a formaldehyde-liberating compound; these elastomers have poor mechanical properties (117). The product prepared from adipic acid, monoethanolamine, and ethylene glycol by modifying with hexamethylene diisocyanate and crosslinking with formaldehyde, is of interest as a vulcanizable polymeric plasticizer for finishes based upon other materials such as polyvinyl formal, nitrocellulose, and cellulose acetate.

Polyester-amide resins made with combinations of adipic acid and maleic anhydride have been patented as insulating enamels for conductors (118,119). Wires insulated with these enamels are reported to have excellent scrape resistance.

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ADRENALIN(E), (HO)₂C₆H₃CH(CH₂NHCH₃)OH. See Epinephrine; Hormones; Psychopharmacological agents.

ADSORPTION

Adsorption, theoretical	421	Adsorption, industrial	459
Bibliography.....	458	Bibliography.....	469

ADSORPTION, THEORETICAL

Adsorption is a technical term coined to denote the taking up (Latin, *sorbere*, to suck up) of gas, vapor, or liquid (the *adsorbate*) by a surface or interface (the *adsorbent*). The term is distinguished from the common word absorption, which refers to the takeup of substances without specifying whether a surface or a bulk phase contains the matter absorbed. The technical word *adsorption* is used, therefore, only when

no doubt exists that the adsorbed matter is held at a surface or an interface. If the interior of a solid is open to invasion by foreign molecules, the takeup is known technically as *sorption*. We may think, therefore, of the surface in its usual sense, or the "surface" may include internal pores that are large enough to admit molecules of adsorbate. Another, and more fundamental, distinction is based on the nature of the bond—whether chemical or physical—by which the adsorbate molecule is attached to the surface. Physical adsorption occurs when molecules are held by van der Waals forces of attraction; chemical adsorption, or *chemisorption*, occurs when the bonds to the surface result from an exchange or a sharing of electrons. De Boer has pointed out that though we have here the distinguishing principle, no easy means is at hand to decide which effect occurs in practice. The opinion is often expressed that the magnitude of the heat of adsorption indicates the kind of adsorption. Generally speaking, one could expect to find that heats of physical adsorption are less than 10 kcal/mole, whereas heats of chemisorption are above 20 kcal/mole. Absolute reliance cannot be placed on this criterion, however, as, occasionally, heats of physical adsorption may be greater than 20 kcal/mole; and, on the other hand, the heat of chemisorption, as of any chemical reaction, may even be negative, as is the case with the heat of formation of endothermic compounds. While it is usually not difficult to decide which of the two types of adsorption is involved, the decision for some examples is far from obvious.

A distinction of a different type is whether the adsorbed atoms or molecules occupy fixed places on the surface (localized adsorption) or are free to move about in two dimensions over the surface (mobile adsorbed film). Both in physical adsorption and in chemisorption the adsorbed film may be either mobile or localized. Everything here depends on the size of the energy barrier to translation along the surface. Migration of the molecules across the surface can always occur, no matter what the type of bonding to the surface, when the adsorbed molecules have enough thermal energy to overcome the energy of activation for migration; at lower temperatures the adsorbed molecules are localized at definite sites on the surface. No sharp natural boundary separates these two types of adsorbed film.

Adsorption at Liquid Surfaces

Adsorption occurs at liquid surfaces, such as the liquid–air surface of a solution or the liquid–liquid interface of an emulsion. The fluidity of liquid substrates precludes the existence of energy barriers to translation of the adsorbed molecules; hence, only mobile adsorbed films are to be found.

An adsorbed film will always form at the interface where two immiscible bulk phases are in contact, except possibly where they are both solid phases. The molecules of the adsorbed material at the interfaces are in dynamic equilibrium with those still in the contiguous bulk phase. This contiguous bulk phase containing the adsorbate may be a gas or vapor, or it may be a pure liquid or a solution. The adsorbed molecules can also be considered as constituting an additional phase at the interface—a two-dimensional phase. The phase rule can be applied to such systems whenever we wish to take into account the presence of two-dimensional phases residing at interfaces; it then has the form

$$P + F = C + 2 + i \quad (1)$$

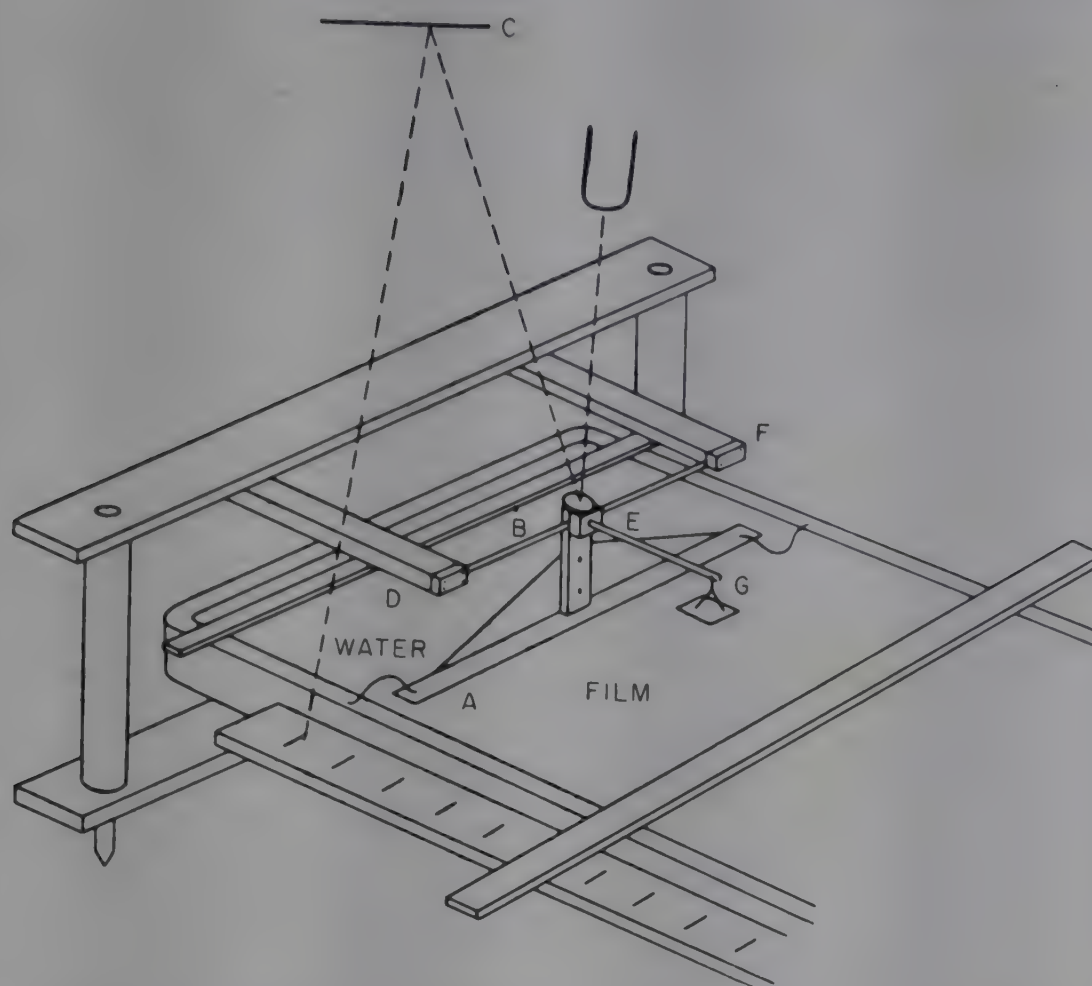


Fig. 1. Diagram of the apparatus for insoluble monolayers at an air-water interface (1). Courtesy A. E. Alexander.

where P , F , and C have their usual meanings of number of phases (including two-dimensional phases), degrees of freedom, and number of components (including components at interfaces), respectively; i is the number of interfaces that we intend to consider. Take the case of the partition of a solute between two immiscible liquids; we have $C = 3$, $P = 3$, and $i = 1$, ie, three components three phases (two bulk and one two-dimensional), and a liquid-liquid interface. For this condensed system,

$$P + F = C + 1 + 1$$

hence $F = 2$; ie, on fixing the temperature and the composition in one of the phases, whether bulk or two-dimensional, the compositions in the remaining two phases are uniquely defined.

The adsorbed film may be spontaneously adsorbed from either or both of the contiguous bulk phases, or it may be a film of a substance that is insoluble in both bulk phases though capable of spreading spontaneously at the interface. This latter type of film includes insoluble monolayers on a liquid surface, of which a well-known example is the oil film spread on water to hinder the breaking of waves. Quantitative measurements of the behavior of such films were initiated in 1891 by Pockels. The apparatus, now known as a film balance, was improved by succeeding investigators, notably Rayleigh, Langmuir, Adam, Alexander, and Guastalla. A modern version of the instrument (1) is shown in Figure 1. The float A, of thin sheet metal, is subjected to a lateral thrust from the surface film; the thrust causes a turning of the bar B, on which a mirror is fixed; a light beam, reflected from the mirror to a second mirror C and thus brought to illuminate a scale, is thereby deflected to a degree proportional to the spreading pres-

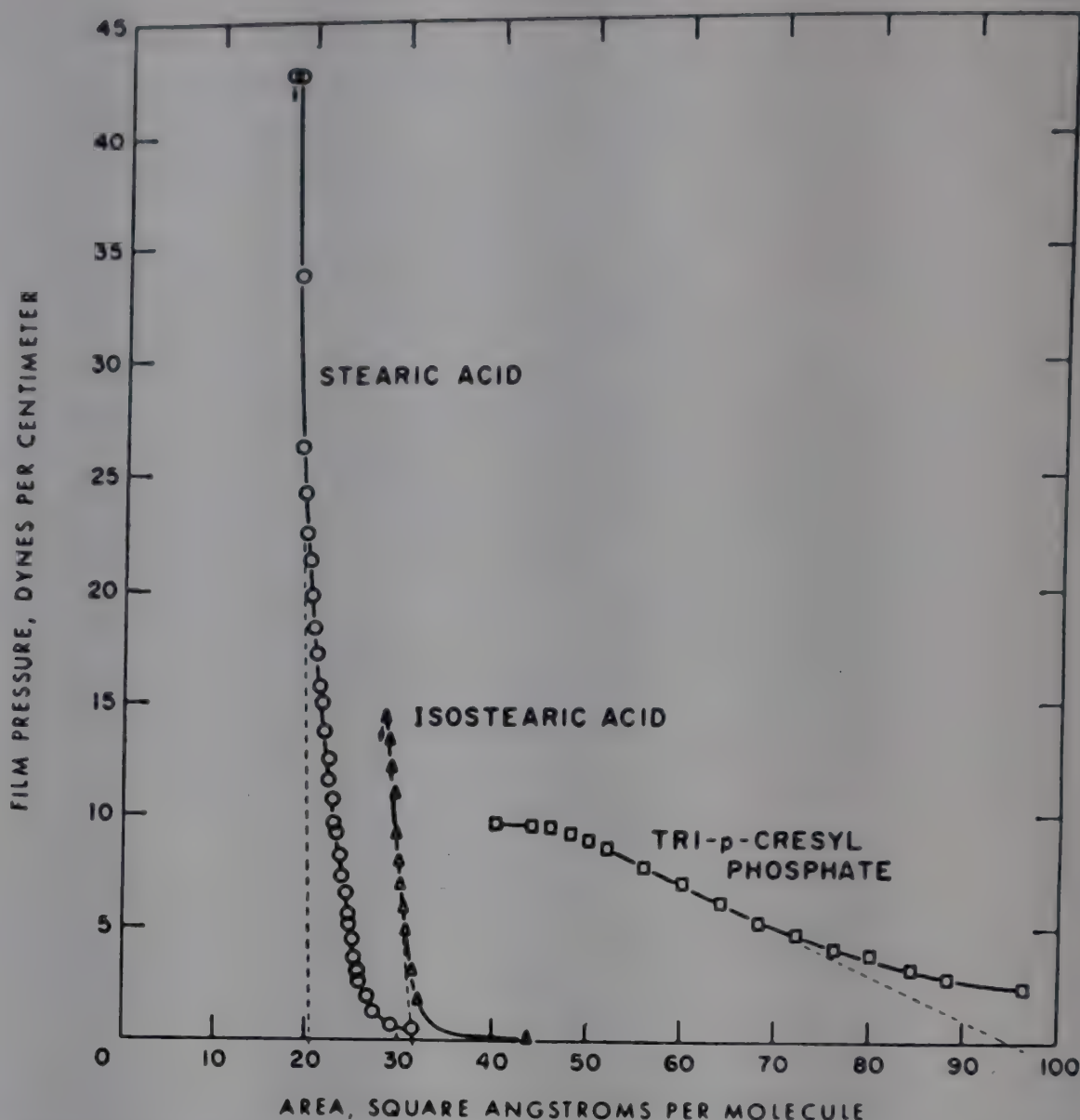


Fig. 2. Pressure-area isotherms for stearic acid, isostearic acid, and tri-*p*-cresyl phosphate. Courtesy H. E. Ries, Jr., and the American Oil Co.

sure of the film. To calibrate the instrument to read absolute units of spreading pressure, π (dynes/cm), standard weights are placed on the pan G, and the resulting deflection of the light beam is measured.

An instrument of this type can be used to obtain the relation between spreading pressure and the area per molecule of the substance in the surface film. A known amount of substance spread as a monolayer on a readily measured area of water surface (thus providing the data for the calculation of σ , the area per molecule), exerts a spreading pressure that can be measured by the instrument, as described above. On compressing the film, by reducing the area of water surface available to it, the spreading pressure increases.

Figure 2 shows the relation between π and σ for some representative monomolecular films on water (2). Pressure-area isotherms are sensitive to small differences in molecular structure. Compare, for example, monolayers of stearic and isostearic acids, whose molecular structures are shown schematically in Figure 3. Stearic acid, which has a straight hydrocarbon chain, gives an extrapolated area of 20 Å² per molecule, compared to 32 Å² for isostearic acid. The methyl side chain at the remote end of a long molecule is the cause of an increase of more than 50% in the molecular area. The two-dimensional pressure at which the monolayer collapses is also affected

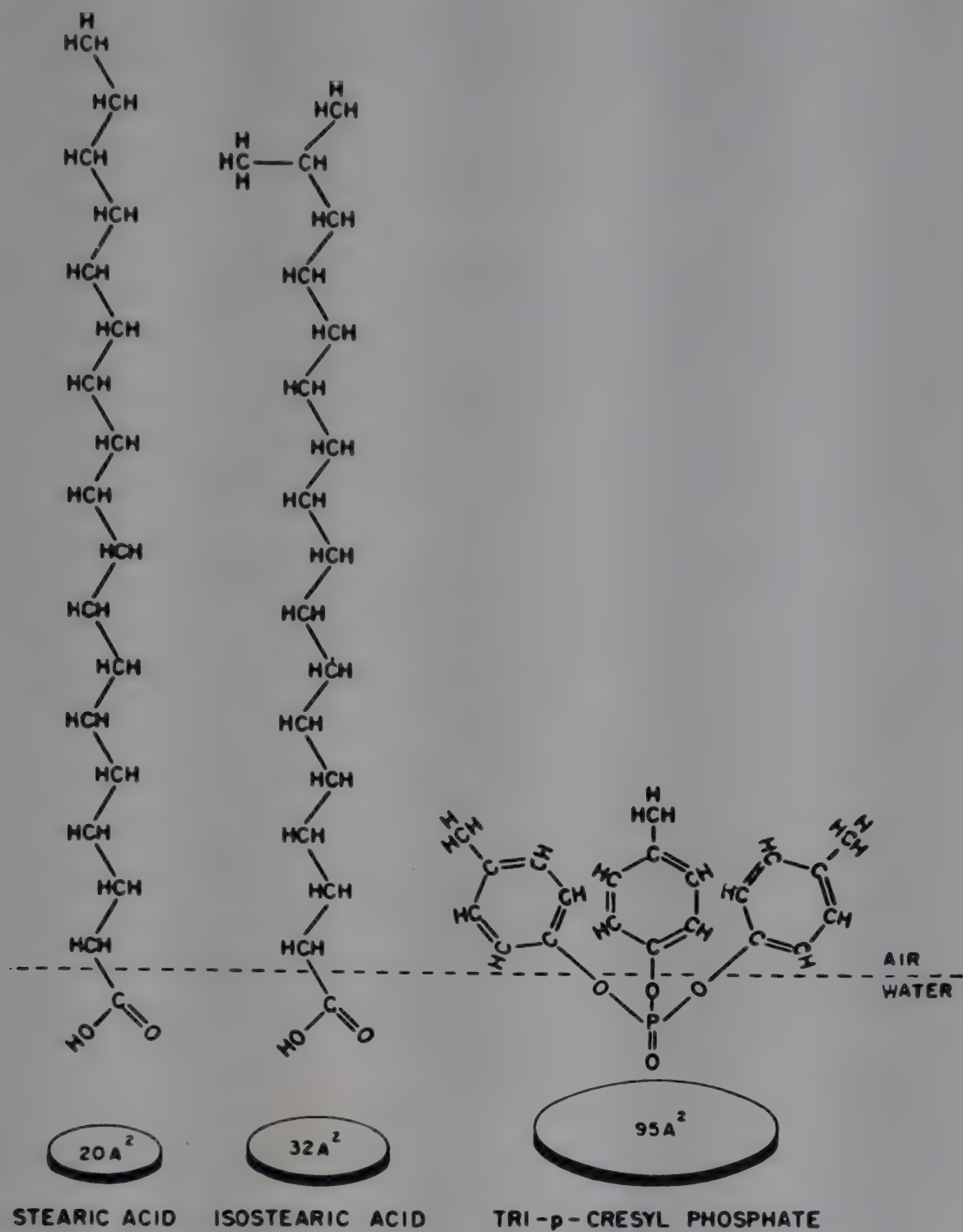


Fig. 3. Molecular structure and orientation of close-packed monolayers on a water surface. Courtesy H. E. Ries, Jr., and the American Oil Co.

by this slight branching of the hydrocarbon chain. The normal stearic acid monolayer can withstand a pressure of 42 dynes/cm before it buckles and collapses; the monolayer of the isomer collapses at only 15 dynes/cm. The two effects are related. The more symmetrical molecules can tolerate higher pressures because they are able to pack together more closely; the branched molecules cannot pack as well and their monomolecular film is therefore more easily crumpled. Tri-*p*-cresyl phosphate shows these effects even more strongly. The molecules are squat and bulky, as shown in Figure 3, and do not readily pack together. The pressure-area isotherm reveals the inability of the monolayer to form a dense, incompressible film; collapse takes place at a low pressure, 9 dynes/cm, and the compressibility, 0.0538 cm/dyne, is more than 25 times that of the stearic acid monolayer. These properties of monolayers are related to the protective action of the agents as rust preventives on metal surfaces.

The more dense and coherent monolayers correlate with better protection by agents; branching of the chain makes the monolayer less coherent and likewise reduces the protecting quality of the agent. The observation that tri-*p*-cresyl phosphate, even at high concentrations, gives no protection against rusting to a metal surface, is therefore consistent with its behavior as an adsorbed insoluble monolayer on the surface of water.

Ries et al. (2) have published a number of interesting and unique electron photomicrographs of insoluble films that had been removed, at different stages of compression, from an aqueous surface. These photographs confirm, by direct vision, that the films are indeed monomolecular; they also show that the condensed film has the form of a two-dimensional dispersion of polymolecular clusters. The molecules that make up the cluster are oriented and tightly packed. Under higher compression the clusters become a continuous phase and, ultimately, just before collapse, completely cover the water surface.

The π - σ - T parameters of an adsorbed film can be related by two-dimensional equations of state, just as the p - V - T parameters of bulk phases. An interesting analog of the pressure-volume relation of a gas is enacted by a single layer of molecules adsorbed at an aqueous surface. An equation of state can be found, which under limiting conditions of area tending to infinity, has the same form as the ideal gas law, ie,

$$\pi\sigma = kT \quad (2)$$

where π is the spreading pressure in dynes/cm, σ is the area per molecule, k is the Boltzmann constant (R/N), and T is the absolute temperature. Equation 2 is called the *two-dimensional ideal gas law*. The behavior of the monomolecular film shows the same kinds of deviation from ideality that are found with gases; the effect of molecular size is to *reduce* the measured area to an actual area available to each molecule, and the effect of intermolecular attraction is to make the measured spreading pressure fall short of the "ideal" value so that a term has to be *added* to it to bring it up to the "ideal" spreading pressure. The proper corrections for nonideal behavior in a monomolecular gaseous film are, therefore, similar to those introduced by van der Waals for an ordinary (three-dimensional) gas.

Two-dimensional phases may exist in more than one state. The molecules at the interface may translate in the same way as molecules of a gas, their motion being restricted, however, to two dimensions. A two-dimensional condensed state can also arise at a temperature less than critical by compressing the two-dimensional gas; the two-dimensional solid state can also be produced. In the course of a two-dimensional phase change, two phases coexist at the same interface, thereby reducing the number of degrees of freedom of the system by one. For example, for the liquid-liquid interface mentioned above, with two bulk and two adsorbed phases, $F = 1$; hence, by applying equation 1, at a given temperature, all the compositions are fixed. The situation closely resembles the more familiar phase changes of bulk matter where a degree of freedom is likewise lost when the two phases coexist.

Another type of adsorption arises at a liquid surface when the adsorbate is dissolved in the liquid. A substance dissolved in a liquid will be present in greater or in less concentration at the surface, compared to its concentration in the bulk phase, depending on whether the surface tension of the solution is thereby lowered below or raised above that of the pure solvent. A thermodynamic relation was derived, in-

dependently, by Gibbs and Thomson; its usual approximate form, applicable to two-component systems at low concentrations, is

$$\Gamma = - \frac{1}{RT} \frac{d\gamma}{d \ln c} \quad (3)$$

where Γ is the excess surface concentration in moles/cm², γ is the surface tension in dynes/cm, and c is the concentration of the solution in moles/cm³. At a liquid surface the experimental measurement of γ is made more readily than that of Γ ; consequently the excess surface concentration at liquid-liquid and liquid-gas interfaces is usually obtained by calculation from surface tension measurements, by means of the Gibbs-Thomson equation. This equation enables us to distinguish between positive and negative adsorption; these terms refer to a positive or a negative surface excess of solute (in other words, the sign of Γ), which is readily detected from the slope of the experimental γ versus $\ln c$ curve, according to equation 3. Ordinary electrolytes in water, at low concentrations, increase the surface tension, which means, as interpreted by equation 3, that they are preferentially retained in the bulk of the aqueous phase. Harkins and McLaughlin calculated that a solute-free layer one molecule thick exists in dilute electrolyte solutions. The forces of solvation of ions is responsible for this behavior. But even methanol, ethanol, and l-propanol, which are positively adsorbed at the water surface at higher concentrations, can show negative adsorption at sufficiently low concentrations (3), at least below about 35°C. This effect is due to the peculiar nature of water; the lower alcohols can, at low enough concentrations, be tolerated as components of the cooperative water structure that exists at temperatures below about 35°C.

Solutes that show pronounced positive adsorption at a liquid surface, as is indicated by their action in lowering surface tension, are called *surface-active agents*. Such substances combine both hydrophilic and lipophilic groups in the same molecule; the hydrophilic portion confers water solubility; and by virtue of the lipophilic group, which has high interfacial energy against water, the solute molecules are retained at the surface, where the interfacial energy is at a minimum. The surface activity of the molecule depends on the size of its lipophilic group, the hydrophilic group being kept constant. One such dependence is formulated quantitatively by Traube's rule: in dilute solutions of the members of any given homologous series, the concentrations required for equal lowering of surface tension decrease by a factor of three for each additional CH₂ group in the molecule. Traube's rule is capable of generalization to apply to adsorption at any type of interface; for any member of a homologous series, the concentration in the bulk phase that is required to provide a given concentration of adsorbed phase at an interface varies geometrically as the length of the molecular chain varies arithmetically; or, even more generally, progressive additions of lipophilic elements to the molecular structure of an adsorbate cause a geometric increase of positive adsorption when the bulk medium is hydrophilic, and a geometric increase of negative adsorption when the bulk medium is lipophilic. The converse rule also holds; hydrophilic elements added to the molecular structure of the adsorbate increase the adsorption out of a lipophilic medium. The quantitative relation expressed by Traube's rule applies only to dilute concentrations in the bulk phases. Adsorption at a liquid surface is made use of in the foam fractionation of surface-active constituents of complex mixtures.

Adsorption of Gases by Solids

THE ADSORPTION ISOTHERM

The solid adsorbent, because of the large surface area that it makes available, is of great practical importance. Unfortunately, we know much less about the behavior of adsorbed films on solid surfaces than of those on liquid surfaces. The liquid substrate offers a uniform field of action for the adsorbed layer since potential inequalities at the surface of a liquid are soon destroyed, thanks to the mobility of its molecules. Any such uniformity of substrate is impossible to achieve with solids; structural deformations are literally frozen into place, and surface contaminations cannot be removed by being dissolved in the bulk adsorbent or by sweeping them away with a surface barrier, as can be done so readily at a liquid surface. We must, accordingly, always keep in mind the existence of a distribution of potentials at every solid substrate, and consider theories that disregard the heterogeneity of the substrate as lacking an essential element in their description of the adsorbed film. Such theories, nevertheless, provide the necessary foundation on which more accurate descriptions can be based.

A gas in contact with a solid is a two-component system with two bulk phases. If adsorption is not taken into account, the ordinary phase rule applies,

$$P + F = C + 2 \quad (4)$$

hence, $F = 2$; ie, two variables, p and T , when specified, determine the state of the system. Let us now consider the solid phase to have two different interfaces, such as might be imagined, for example, for a crystal with two different crystal faces. Taking into account adsorption at these interfaces, $i = 2$. The total number of phases, bulk and surface, makes $P = 4$; hence, by equation 1, $F = 2$. The two variables, p and T , when specified, determine the state of the system, which means that the surface concentration at each of the two interfaces is fixed at a given temperature and pressure. The same conclusion is true for any number of interfaces on the same solid substrate; let $i = i$, then $P = 2 + i$, and $F = 2$. No matter how many separate types of surface are present, the surface concentration at every one is simultaneously determined at a given temperature and pressure. This conclusion is pertinent to real adsorption systems, where a single adsorbent invariably has many different surfaces, which may be caused by different crystal faces or even by surface contamination. Each of the surfaces, with a different atomic arrangement, creates a different environmental force field for a visiting molecule, thus producing interfacial phases of different concentrations. The situation is analogous to the partition of a single solute between a number of immiscible solvents; each separate surface acts as if it were a different "solvent" for the adsorbate.

The conclusion that the surface concentration at each and every surface is determined by p and T only justifies our use of the adsorption isotherm as a description of the equilibrium state of the system. The adsorption isotherm describes the variation of the amount of gas adsorbed with its concentration (ie, pressure) in the bulk phase, at constant temperature. The measured amount adsorbed is, of course, the sum of all the amounts at all the different surfaces of the adsorbent; as each of the members of this sum is determined by p and T , the sum itself is also thus determined.

The ultimate aim of the theory of adsorption is to describe the substrate in terms of all the different surfaces of which it is composed; at present, however, we are still

a long way from this goal. The earliest attempts at reaching a mathematical description of the dynamic equilibrium between the gas and the adsorbed phases were entirely empirical. A parabolic equation of the following form was found to be suitable.

$$\frac{x}{m} = kp^{1/n} \tag{5}$$

where x is the grams of adsorbate per m grams of adsorbent, p is the pressure of the bulk adsorbate phase, k and n ($n > 1$) are empirical constants. This equation, although not original with Freundlich, was so extensively used by that writer that it now bears his name. The Freundlich equation cannot, however, by its very nature, be a perfect representation of the physical reality, as it states that the value of x/m increases without limit as p increases; whereas in actuality the saturation of the surface with a monomolecular layer quite often sets an upper limit to the concentration in the two-dimensional phase.

Langmuir produced in 1916 the first theoretical treatment of an isothermal adsorption equilibrium. According to Langmuir, the rate of adsorption, u , is proportional (a) to the number of molecules that strike 1 cm² of surface per second, (b) to the fraction, f_1 , of that number that remain on the surface long enough for an exchange of kinetic energy to take place, and (c) to the fraction of the 1 cm² of surface not already occupied by adsorbed molecules. Expressed analytically,

$$u = \frac{pN}{\sqrt{2\pi MRT}} f_1(1 - \theta) \tag{6}$$

where M is the molecular weight of the adsorbate, and θ is the fraction of the adsorbent surface covered with adsorbate. The rate of desorption, v , is proportional to the fraction of the surface occupied by adsorbate, and to the fraction of the adsorbed molecules that have enough energy to leave the attractive forces of the surface, which are expressed as a uniform adsorptive energy of U kcal/mole. Hence,

$$v = k_0 \theta e^{-U/RT} \tag{7}$$

At equilibrium $u = v$, from which we obtain

$$p = K \frac{\theta}{1 - \theta} \tag{8}$$

where

$$K = \frac{k_0}{f_1} \frac{\sqrt{2\pi MRT}}{N} e^{-U/RT} = Ae^{-U/R} \tag{9}$$

The concept underlying the use of θ , which is defined as the fraction of the surface covered by an adsorbed film, implies that when $\theta = 1$ the whole surface of the solid is covered with a monomolecular film. Let $\theta = V/V_m$, where V is the amount of gas adsorbed at an equilibrium pressure p , and V_m is the amount adsorbed at surface saturation. Equation 8 then becomes

$$p = \frac{KV}{V_m - V} \tag{10}$$

in which the experimentally measured quantities are p and V , and V_m and K are constants that can be evaluated if the experimental data are capable of being described by equation 10.

Equation 10 is called the Langmuir adsorption isotherm. Implicit in its development are the following assumptions about the model:

1. The adsorption in the bulk gaseous phase behaves as an ideal gas.
2. The amount adsorbed is confined to a monomolecular layer.
3. Every part of the surface has the same energy of adsorption.
4. No adsorbate-adsorbate interaction is taken into account; presumably it is negligible.
5. The adsorbed molecules are localized; ie, they have definite points of attachment to the surface. This assumption is made explicit only in the statistical derivation of the Langmuir equation, such as that given by Fowler and Guggenheim (4). These authors state that nonstatistical derivations of the Langmuir equation make assumptions about the mechanism of sorption and desorption, and that these assumptions are not strictly required. Equation 10 "must hold whatever the kinetics of the processes, provided only that the molecules are adsorbed on to definite sites and do not interact with one another" (4).

The first two of the preceding assumptions are acceptable as true of many gas-solid systems; but the second and third assumptions are always false. No solid surface is ever ideally uniform: even in the absence of different crystalline faces or adventitious impurities, some nonuniformity is introduced by edges and corners, cracks, dislocations, and other crystal imperfections. Also the assumption that at all surface concentrations the adsorbate-adsorbate interaction is negligible is never correct: even a noble gas has enough energy of interaction to account for about 25% of the measured heat of adsorption at half saturation of the surface. The effect of surface nonuniformity is to cause the energy of adsorption to decrease with θ , whereas the effect of adsorbate-adsorbate interaction is to cause it to increase. The net result of the two erroneous assumptions is, therefore, partially to cancel out each other's effects; the success, not always deserved, of the Langmuir equation as a description of the adsorption isotherm owes much to this coincidence. In spite of its grave faults, however, the development of the Langmuir model was of prime importance in the history of the subject, because it named for the first time the factors that are significant in the process of adsorption; all subsequent theories have used the concepts and the terminology introduced by Langmuir.

With the possibility of evaluating the saturation capacity, V_m , of a surface in terms of a monomolecular layer, a practical application of the adsorption isotherm became obvious, namely, the measurement of the degree of subdivision of a solid in terms of its specific surface. The solid is used as the adsorbent; V_m once determined, all that is then required is a definitive value for the molecular cross-sectional area, σ_0 , of the adsorbate; the specific surface of the solid adsorbent, Σ , in m^2/g then follows

$$\Sigma = (V_m/22,400) \times N \times \sigma_0 \times 10^{-20}$$

where V_m is in cc of adsorbate (measured as if at STP) per gram of adsorbent, N is Avogadro's number, and σ_0 is the molecular cross section of adsorbate in $\text{\AA}^2/\text{molecule}$.

A convenient practical measurement of an adsorption isotherm is possible with nitrogen as adsorbate, at the temperature of its boiling point, 77.5°K . Liquid nitrogen is readily available for use as a thermostat liquid, and the gas itself is easily ob-

tained in a high state of purity. But this choice of conditions, so convenient for practice, introduces new difficulties in the theory: at 77.5°K nitrogen is not a gas but a vapor; the adsorption, therefore, is multimolecular rather than monomolecular, and the Langmuir equation, which contains the constant we want to measure, is applicable only to the low-pressure portion of the isotherm at which the adsorbed film is monomolecular. The theory was extended in 1938 by Brunauer, Emmett, and Teller (5), whose model of multimolecular adsorption, known as the B-E-T theory, postulated a number of simultaneous Langmuir-type adsorptions between each two successive molecular layers. A few assumptions had to be added to the model in order to simplify the mathematical treatment, namely that the energy of adsorption to the bare solid surface is uniform and characteristic of the solid; that the energies of adsorption in the second and succeeding layers of adsorbate are also uniform, and are all equal to the heat of liquefaction of the adsorbate. The final expression of the B-E-T theory is

$$V = \frac{V_m C p}{(p_0 - p)[1 + (C - 1)(p/p_0)]} \quad (11)$$

where p_0 is the saturation vapor pressure of the adsorbate and V_m and C are constants; V_m has the same significance in the B-E-T theory as it has in the Langmuir theory.

The B-E-T theory is the basis of a method of measuring the specific surface of a solid, using the value of V_m derived from equation 11. This method has been experimentally shown to be sufficiently accurate for most practical purposes and has successfully met an urgent requirement for a rapid estimate of particle size. By so doing it has made possible great advances in both theoretical and practical studies of surface chemistry and physics. We must not, however, confuse the triumphs of the B-E-T theory in this practical application with its claims as a model of the adsorption process; in this latter respect it is obviously far from satisfactory. The Langmuir model with its two unjustifiable assumptions, the effects of which fortuitously cancel each other, is the basis of the B-E-T model, and the additional assumptions introduced in the B-E-T derivation merely add further improbabilities to the total picture. At the present time, in fact, an adequate model of multimolecular adsorption could hardly be produced, as no adequate model of the simpler phenomenon of monomolecular adsorption is yet available. Such a model, if it is to gain our intellectual assent, will have to take into account both heterogeneity of the underlying solid substrate and also the variation of adsorbate-adsorbate interaction with surface concentration.

The fifth assumption implicit in the Langmuir isotherm introduced the concept of localization. As defined by the requirements of the statistical derivation, localization excludes any lateral movement of the adsorbed molecules; ie, molecules are adsorbed by and desorbed from specific sites on the surface. The adsorbed molecules still have thermal energy, which must therefore manifest itself in three degrees of vibrational freedom about the site. The energy required for a molecule to move from site to site is the same as that required for desorption into the gas phase so that there is no difference in localized adsorption between translation along the surface and the desorption.

MOBILE AND LOCALIZED ADSORBED FILMS

The surface of a solid is not a continuum but a two-dimensional array of atoms that causes maxima and minima in the interaction energy as a molecule moves along the surface. If the depth of these potential wells is equal to the energy for desorption we have the condition for a localized film; but we could imagine the situation where the

energy required for a molecule to move from site to site is less than that required for its escape into the gas phase. Instead of using the concept of a site, which implies a fixed point of attachment to the surface, it would now be more exact to think of an energy barrier to translation along the surface. The important point is, however, that the molecule can move laterally within the two-dimensional phase and desorption can take place from any point on the surface. This kind of adsorbed film is called mobile.

No sharp natural boundary separates the two types of adsorbed film. The height of the energy barrier for total desorption from the surface may be only slightly greater than the energy barrier to translation. A molecule whose kinetic energy was in the narrow range between these two energy limits could translate without leaving the two-dimensional phase, but such molecules would be only a small fraction of those adsorbed; consequently, the effective adsorption equilibrium would be that of localized adsorption.

The energy barriers, whether to translation or to desorption, are not temperature dependent but are properties of the adsorbate-adsorbent system. The number of molecules with energies greater than the energy barrier to desorption, P , increases with temperature; these are the molecules in the process of desorbing into the gas phase. The number of molecules having energies less than the barrier to translation, χ , decreases with temperature; these molecules remain vibrating about fixed sites on the substrate. Molecules with energy in the range between χ and P are confined to the two-dimensional phase but have translational freedom within it. The ratio of translating to nontranslating molecules increases with temperature to a limiting value given by

$$\frac{\text{tr}}{\text{nontr}} = \frac{(e^{-\chi/RT} - e^{-P/RT})}{1 - e^{-\chi/RT}}$$

When χ is equal to P , no molecules are translating in the two-dimensional phase, ie, the adsorbed film is localized. When χ is close to P , only a small fraction of the molecules can translate and the film is effectively localized. When χ is much less than P , most of the adsorbed molecules can translate freely except at very low temperatures. In physical adsorption the adsorbed film generally is mobile, as in most cases χ would be very much less than P . Nevertheless at very low temperatures, most of the molecules are in the nontranslating state; we might call this condition *quasi-localized*. It is not true localization because there are still more molecules able to translate than are able to desorb, and an equilibrium distribution of molecules can be reached within the two-dimensional phase. The kinetic properties of the film are the same as in true localization, but the equilibrium mechanism is not. When the molecule is localized on a heterogeneous substrate, it cannot spontaneously reduce the free energy of the interface by moving along the surface to a lower energy state; equilibrium can only be reached by desorption and chance readsorption in a lower energy state, at which it is held for a longer period of time. The attainment of dynamic equilibrium, therefore, is apt to be a slow process in localized adsorption. The mobile film, on the other hand, can reach the state of minimum free energy more readily and more rapidly. In chemical adsorption the adsorbate is not necessarily localized, although that condition would be expected to be more prevalent than for physical adsorption. But much evidence exists for mobility of chemically adsorbed molecules on certain substrates, for example, on metal surfaces, where it is due to the "fluidity" conferred by electron resonance in the lattice.

PHYSICAL ADSORPTION

Much of the recent work on physical adsorption is devoted to the low-pressure portions of the adsorption isotherm. Multilayer theories, such as the B-E-T, have proved their utility in leading to the measurement of specific surface areas; but further information about the solid substrate can be elicited more readily when adsorption in the second or succeeding layers is not present as an extra complexity. More searching and fundamental descriptions of the dynamic equilibrium between the gas and the adsorbed phase are essential. The method of deriving an adsorption isotherm equation by means of a kinetic mechanism, such as was done for the Langmuir and the B-E-T equations, does not readily lend itself to the introduction of all the necessary conditions that one would like to take into account for a complete description of the adsorption process. The methods of statistical mechanics have been used by several theorists to provide more sophisticated pictures of adsorption; an example of these results is the finding that a mobile adsorbed film on a homotactic substrate can be described by a two-dimensional virial equation of state.

$$\pi = kT \left[\frac{1}{\sigma} + \frac{B(T)}{\sigma^2} + \frac{C(T)}{\sigma^3} + \frac{D(T)}{\sigma^4} \dots \right] \quad (12)$$

The Gibbs-Thomson equation (eq. 3) can be written for the gas-solid adsorption equilibrium in terms of the equilibrium pressure of the gas, p , and the fraction of the surface covered, θ . The quantity θ is defined by σ_0/σ , where σ_0 is the limiting area per molecule at infinite compression and σ is the area per molecule at the equilibrium condition defined by p and T . Expressed in terms of this system, equation 3 becomes

$$d\pi = \frac{kT}{\sigma_0} \theta d \ln p \quad (13)$$

Let the two-dimensional equation of state, such as that exemplified in equation 12 above, be written generally as

$$\pi = \frac{kT}{\sigma_0} f(\theta, T) \quad (14)$$

then at constant T ,

$$d\pi = \frac{kT}{\sigma_0} f'(\theta, T) d\theta \quad (15)$$

Combining equations 13 and 15 gives

$$d \ln p = f'(\theta, T) d \ln \theta$$

therefore,

$$\ln p = \int_0^\theta f'(\theta, T) d \ln \theta + \ln K \quad (16)$$

where K is an integration constant, hence not dependent on θ , but certainly temperature-dependent. Equation 16 is the instrument by which a two-dimensional equation of state, expressed as equation 12 above, can be transformed into its equivalent adsorption isotherm equation, in terms of p , θ , and K . Expressed even more generally it is

$$\ln p = \ln K + \ln g(\theta, T)$$

where

$$\ln g(\theta, T) = \int_0^\theta f'(\theta, T) d \ln \theta \quad (17)$$

The constant K reflects the adsorptive potential of the solid surface. Its nature can be better appreciated by the following argument: the integral standard change of free energy of an isothermal adsorption process for one mole of gas in its standard state (760 mm) to the adsorbed state at a standard surface concentration θ_s and equilibrium pressure p_s is

$$\Delta G_s^{\text{ads}} = RT \ln \frac{p_s}{760} \quad (18)$$

or

$$\Delta G_s^{\text{ads}} = RT \ln K + RT \ln g'(\theta_s, T) - RT \ln 760 \quad (19)$$

Also

$$\Delta G_s^{\text{ads}} = \Delta H_s^{\text{ads}} - T \Delta S_s^{\text{ads}} \quad (20)$$

where ΔH_s^{ads} is the standard integral enthalpy change of the adsorption process. Hill (6) has shown that ΔH^{ads} is properly defined by the relation,

$$\left(\frac{\partial \ln p}{\partial T} \right)_\pi = - \frac{\Delta H^{\text{ads}}}{RT^2} \quad (21)$$

whereas the differential isosteric heat of adsorption, q^{st} , is defined by

$$\left(\frac{\partial \ln p}{\partial T} \right)_\theta = \frac{q^{\text{st}}}{RT^2} \quad (22)$$

The difference in sign between equations 21 and 22 is the result of a conventional usage in this subject by which the heat liberated on adsorption is taken as positive; the thermodynamic convention is the opposite one, in which heat *absorbed* is positive. The relation between ΔH^{ads} and q^{st} is not a simple one, being given in fact by

$$\Delta H^{\text{ads}} = -q^{\text{st}} + \frac{T\sigma_0}{\theta} \left(\frac{\partial \pi}{\partial T} \right)_\theta \quad (23)$$

The standard state of the adsorbed film is conventionally taken as that state where at 0°C the average distance between the molecules is the same as in the three-dimensional standard state (0°C, 760 mm). This defines the value of $\sigma_s = 4.08T \times 10^{-16}$ cm²/molecule adsorbed. At this low surface concentration the two-dimensional ideal gas law (eq. 2) is applicable; hence,

$$\pi_s = \frac{kT}{\sigma_s} = \frac{\theta_s}{\sigma_0} RT \quad (24)$$

The value of π_s thus derived is 0.338 dynes/cm.

Using equation 24 to define the standard state, we find that

$$\Delta H_s^{\text{ads}} = -q_s^{\text{st}} + RT = -q_s^{\text{diff}}$$

$$p_s = K\theta_s$$

$$\ln g(\theta_s, T) = \ln \theta_s$$

therefore,

$$\ln K = -\frac{q_s^{\text{diff}}}{RT} - \frac{\Delta S_s^{\text{ads}}}{R} - \ln \theta_s + \ln 760$$

or

$$K = A \exp (-q_s^{\text{diff}}/RT) \tag{25}$$

where

$$\ln A = -\frac{\Delta S_s^{\text{ads}}}{R} - \ln \theta_s + \ln 760 \tag{26}$$

Since K is independent of θ , it cannot contain any term related to adsorbate-adsorbate interaction, which is θ -dependent. It refers, in fact, only to the interaction between adsorbate and adsorbent and so has particular importance for the measurement of the adsorptive potential of a solid surface as revealed by q_s^{diff} , and the kinetic state of the adsorbed molecule, as revealed by $-\Delta S_s^{\text{ads}}$.

All the isotherm equations that we have discussed hitherto are postulated on the assumption that the solid surface reveals a uniform adsorptive potential over all its extent. A pressing problem is to determine the form of the adsorption isotherm for a surface that has a distribution of adsorptive potentials.

For the purpose of such a theory, an adsorption potential energy function that is characteristic of the system and independent of temperature is desirable. Such a quantity, designated U_0 , is conveniently defined by the potential energy difference between the lowest energy state of a molecule in the gas phase and its lowest energy state in the adsorbed phase, both at infinite dilutions. To develop this function, let ${}_gP^{\text{ads}}$ be the potential energy per mole for adsorption of a gas molecule; then, for an ideal gas, the total energy per mole, kinetic and potential, of a molecule in the gas phase, ${}_gE$, is given by

$${}_gE = {}_gP^{\text{ads}} + {}_gE^{\text{kin}} \tag{27}$$

where ${}_gE^{\text{kin}}$ is the total kinetic energy per mole of a molecule in the gas: thus ${}_gE^{\text{kin}} = \frac{3}{2} RT$ for an ideal monatomic gas. Let ${}_aE^{\text{vib}}$ be the average vibrational energy per mole of a molecule in an adsorbed film; then, for a mobile adsorbed film, the total energy (excluding adsorbate-adsorbate interaction) per mole of a molecule in the surface film, ${}_aE$, is given by

$${}_aE = {}_aE^{\text{vib}} + {}_aE^{\text{kin}} \tag{28}$$

where ${}_aE^{\text{kin}}$ is the kinetic energy of translation and rotation of the adsorbed molecule. The total energy change on adsorption is

$${}_gE - {}_aE = {}_gP^{\text{ads}} - {}_aE^{\text{vib}} - \Delta E^{\text{kin}} \tag{29}$$

where

$$\Delta E^{\text{kin}} = {}_aE^{\text{kin}} - {}_gE^{\text{kin}} \tag{30}$$

Then

$${}_gE - {}_aE = ({}_gP^{\text{ads}} - {}_aE_0^{\text{vib}}) - ({}_aE^{\text{vib}} - {}_aE_0^{\text{vib}}) - \Delta E^{\text{kin}} \tag{31}$$

where ${}_aE_0^{\text{vib}}$ is the zero-point vibrational energy of the adsorbed molecule, equivalent to $Nh\nu/2$, where ν is the vibrational frequency of the adsorbed molecule (assumed to be an harmonic oscillator) with respect to the surface. We defined U_0 as the difference in potential energy of a molecule in its lowest energy state in the gas, ie, when ${}_gE^{\text{kin}} = 0$; and its zero-point vibrational level, ${}_aE_0^{\text{vib}}$ in the adsorbed phase on the surface; therefore,

$$U_0 = {}_gP^{\text{ads}} - {}_aE_0^{\text{vib}} \quad (32)$$

and

$${}_gE - {}_aE = U_0 - ({}_aE^{\text{vib}} - {}_aE_0^{\text{vib}}) - \Delta E^{\text{kin}} \quad (33)$$

We shall now relate U_0 to the more familiar heats of adsorption: q^{diff} , the differential heat of adsorption, and q^{st} , the isosteric heat of adsorption, which have been defined and discussed by Hill (6).

$$q^{\text{diff}} = {}_gE - {}_aE - \theta \left[\frac{\partial({}_aE)}{\partial\theta} \right]_{T,\Sigma} \quad (34)$$

and

$$q^{\text{st}} = q^{\text{diff}} + RT \quad (35)$$

For the particular case of a two-dimensional van der Waals gas as the adsorbed phase, and a homotattic substrate,

$$\left[\frac{\partial({}_aE)}{\partial\theta} \right]_{T,\Sigma} = -\frac{\alpha}{\beta} \quad (36)$$

hence

$$q^{\text{diff}} = {}_gE - {}_aE + \frac{\alpha\theta}{\beta} \quad (37)$$

Integrating equation 36 between limits gives

$$\int_{{}_aE}^{{}_gE} d({}_aE) = -\frac{\alpha}{\beta} \int_0^\theta d\theta = -\frac{\alpha\theta}{\beta}$$

hence

$${}_aE = {}_gE - \frac{\alpha\theta}{\beta} \quad (38)$$

Combining equation 38 with equations 33 and 37 gives

$$q^{\text{diff}} = {}_gE - {}_aE + \frac{2\alpha\theta}{\beta} = U_0 - ({}_aE^{\text{vib}} - {}_aE_0^{\text{vib}}) - \Delta E^{\text{kin}} + \frac{2\alpha\theta}{\beta} \quad (39)$$

and

$$q^{\text{st}} = q^{\text{diff}} + RT = U_0 - ({}_aE^{\text{vib}} - {}_aE_0^{\text{vib}}) - \Delta E^{\text{kin}} + RT + \frac{2\alpha\theta}{\beta} \quad (40)$$

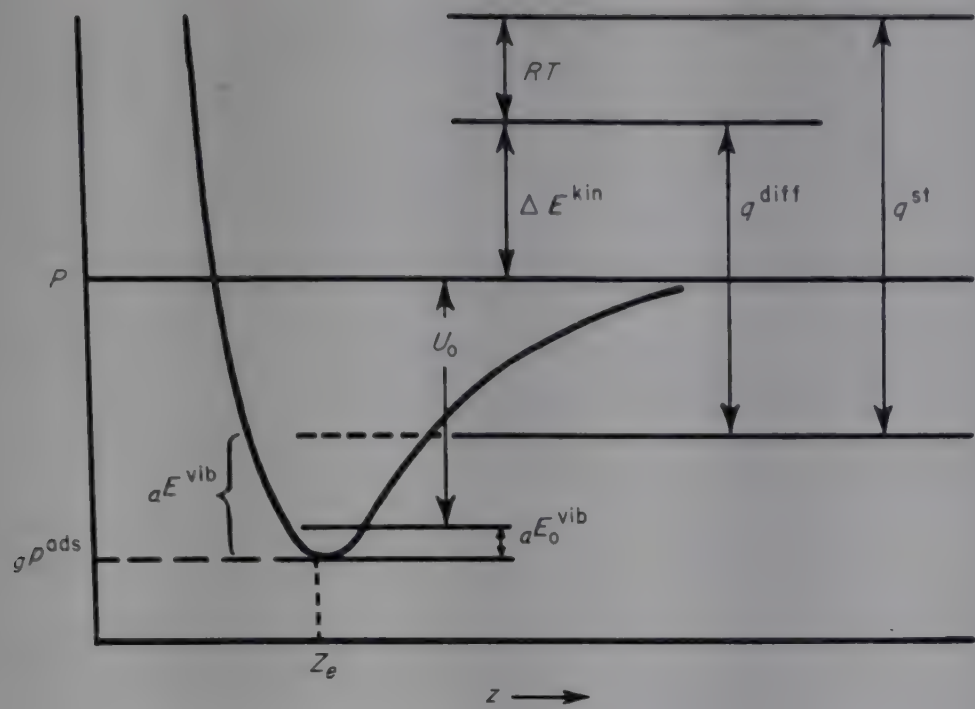


Fig. 4. The potential well for adsorbate-adsorbent interaction as a function of distance from the surface, showing the relation of the various heats of adsorption.

if we assume ${}^p_gE = {}^0_gE$ (true for most gases). The relations between U_0 and other potential energy functions of adsorption are shown in Figure 4, where the loss of potential energy of a gas molecule is plotted as a function of its approach to the substrate. This diagram leaves out of account the adsorbate-adsorbate interactions. The values of q^{diff} or q^{st} shown in the diagram refer, therefore, to their limiting values, θ tending to zero; a θ -dependent term would be added to these values to obtain q^{diff} as defined by Hill in equation 34.

The expressions for K , equations 25 and 26, can now be translated into terms of U_0 , by combining equations 25 and 39. This allows us to write

$$K = A^0 \exp (- U_0/RT) \tag{41}$$

where

$$\ln A^0 = - \frac{\Delta S_s^{\text{ads}}}{R} + \left(\frac{{}_aE^{\text{vib}} - \frac{1}{2} N h \nu}{RT} \right) - \frac{\Delta E^{\text{kin}}}{RT} - \ln \theta_s + \ln 760 \tag{42}$$

For the low value of θ used to define the standard state of the adsorbed phase, the term $2\alpha\theta_s/\beta$ is considered negligible.

Having defined U_0 and illustrated its significance, we now apply it to determine the form of the adsorption isotherm for a heterogeneous surface, ie, one that has an unknown distribution of adsorptive potential energies (U_0). In its most general form this problem can be expressed as the solution of the equation

$$\theta = \int_e^g \Phi(U_0) \Psi(p, U_0) dU_0 \tag{43}$$

where θ is the relative surface concentration of the adsorbate. The fraction, $d\delta_i$, of the total surface Σ that has a potential energy for adsorption U_{0i} is $\Phi(U_0) dU_0$: in other words, $\Phi(U_0) dU_0$ describes the distribution of the adsorptive energies that exists for a given adsorbate on a given adsorbent. The amount of surface that has an adsorptive energy U_{0i} is $\Sigma d\delta_i$; this patch of surface is treated as homotattic for ad-

sorption and the whole surface is considered as composed of a large number of such homotattic patches, each with its own adsorptive energy. (The term *homotattic* was introduced by Sanford and Ross (7), who defined a homotattic surface as the surface of a submicroscopic patch or region, part of a larger surface, which acts as if its structure were uniform and homogeneous.) The fraction θ_i of a given patch that is covered by adsorbate molecules at an equilibrium pressure p is described by the function $\Psi(p, U_0)$; in other words, $\Psi(p, U_0)$ is the adsorption isotherm for a homotattic patch of adsorptive energy U_{0i} . In writing equation 43 we implicitly assumed that the adsorption equilibrium pertaining to every patch on the surface can be described by an adsorption isotherm of the same form; if some portions of the surface, however, cause, for example, localized adsorption of an adsorbate, whereas other portions interact with the adsorbate in a different manner, the same function $\Psi(p, U_0)$ would not hold for every patch. Another special case arises when two or three different kinds of solid substrate are present together as, for example, with crystals containing well-defined crystalline faces. Here, each crystalline face is likely to show a separate, narrow distribution of U_0 values, superimposed on a more general distribution due to elements of surface heterogeneity that have in practice hitherto proved impossible to eliminate entirely. Special cases of these types, if the distinctions between the operating functions are sufficiently well marked, can be treated by considering equation 43 as the sum of two or three similar terms, each term referring to different constituents of the total surface.

Equation 43 is a general expression for the adsorption isotherm. It becomes a specific description only when a choice has been made for the functions $\Phi(U_0)$ dU_0 and $\Psi(p, U_0)$. This choice will be determined by the nature of the model that we select; and the selection will be determined by what is considered to be the best description of the physical reality. Fortunately the shape of the adsorption isotherm is not too sensitive to variations in the mathematical form of the distribution function, as long as a reasonable approximation to a unimodal description is provided. This statement is based on the successful descriptions provided of a number of experimental adsorption systems by using a symmetrical distribution function (Gaussian), although this function is not likely to be precisely true for all of them.

The Gaussian probability function used for the distribution of adsorptive potentials of the surface has the form,

$$d\delta_i = \Phi(U_0)dU_0 = \frac{1}{n} \exp [-\gamma(U_0 - U_0')^2] dU_0 \quad (44)$$

where U_0' is the average adsorptive potential energy and γ determines the width of the distribution; n is a normalizing factor required to make $\int_e^\theta d\delta_i = 1$. The adsorption isotherm, equation 43, then has the form

$$\theta = \frac{1}{n} \int_e^\theta \theta_i \exp [-\gamma(U_0 - U_0')^2] dU_0 \quad (45)$$

where θ_i is derived from the equation of state pertaining to each patch.

The simplest such equation of state is the two-dimensional ideal gas law, which would describe the adsorbed phase at very low surface concentrations. This application is by no means a trivial one. Halsey and his coworkers (8) at the University of Washington have reported a series of adsorption isotherms, measured with a pre-

cision that is of an order of magnitude greater than any achieved hitherto; the data refer to concentrations less than 10% of the monolayer. These authors have analyzed the data by means of a treatment based on virial coefficients to yield interaction energies and surface area, but prior to sophisticated analyses based on statistical mechanics the system should be described in terms of the simple concepts developed above. The isotherms at these low surface concentrations are all straight lines; therefore on each homotattic patch of the surface, defined by its adsorptive potential U_{0i} , the adsorbed film at sufficiently low surface concentration is described by the isotherm equation

$$p = K_i \theta_i \quad (46)$$

where

$$K_i = A_i^0 \exp (-U_{0i}/RT) \quad (47)$$

We now assume that A_i^0 has the same value for every patch ($A_i^0 = A^0$). The evaluation of A^0 (eq. 42) shows that this assumption puts the same vibrational frequency of the adsorbed atom on every surface patch; this description of behavior is not exactly true, but it is not seriously in error except for surfaces of extreme heterogeneity. Equation 45 then becomes, for the Henry's law (ie, the linear) region of the adsorption,

$$\theta = \frac{p}{nA^0} \int_e^{\theta} \exp \left[-\gamma(U_0 - U_0')^2 + \frac{U_0}{RT} \right] dU_0$$

which, on integration, becomes

$$\theta = \frac{p}{K'} \exp \left(\frac{1}{4\gamma(RT)^2} \right) \quad (48)$$

where K' is defined in terms of the most frequent adsorptive potential U_0' by

$$K' = A^0 \exp (-U_0'/RT) \quad (49)$$

In summary, the above argument states that, when Henry's law applies to any energetically distinct surface patch, as must be true at sufficiently low total surface concentration, the adsorption isotherm, even for a heterogeneous surface, is a straight line through the origin, described by equation 48. Let the slope of this line, dV/dp , equal Z , where V is the amount adsorbed at an equilibrium pressure p ; then $V = Zp$. The relative surface concentration θ is defined by V/V_β where V_β is the monolayer capacity of the surface when the adsorbed molecules are compressed to an area equal to that of the two-dimensional van der Waals constant β . The experimentally determined limiting slope of the adsorption isotherm can now be expressed in terms of theory,

$$Z = \frac{V_\beta}{K'} \exp \left(\frac{1}{4\gamma(RT)^2} \right) \quad (50)$$

hence,

$$\ln Z + \ln A^0 = \frac{U_0'}{RT} + \ln V_\beta + \frac{1}{4\gamma(RT)^2} \quad (51)$$

Equation 51 expresses the significance of the slope of the Henry's law portion of the adsorption isotherm: it is clearly a complex function, including $\ln A^0$ which is

defined by equation 42 and contains the entropy change on adsorption, the monolayer capacity of the surface, V_β , and the degree of adsorptive heterogeneity, γ . Consider, as a model of the adsorbed film, that molecules are able to translate freely parallel to the substrate and are also vibrating as harmonic oscillators normal to the substrate; the term ΔS_s^{ads} , therefore, includes both the entropy change corresponding to the loss of one degree of translational freedom and that due to the added vibration gained on adsorption,

$$\Delta E^{\text{kin}} = -\frac{1}{2} RT \quad (52)$$

and

$$\Delta S_s^{\text{ads}} = \Delta S_s^{\text{tr}} + {}_a S^{\text{vib}} \quad (53)$$

where

$${}_a S^{\text{vib}} = \frac{{}_a E^{\text{vib}} - \frac{1}{2} N h \nu}{T} - \frac{{}_a G^{\text{vib}} - \frac{1}{2} N h \nu}{T} \quad (54)$$

For ΔS_s^{tr} one can use the Sackur-Tetrode equation to compute the loss of one degree of translational freedom, by means of which the expression for the entropy change on adsorption is

$$-\Delta S_s^{\text{tr}} = {}_g S_s^{\text{tr}} - {}_a S_s^{\text{tr}} = \frac{1}{2} R \ln M + \frac{1}{2} R \ln T + 2.31 \quad (55)$$

Making use of these equations, equation 42 becomes for this model

$$\ln A^0 = -\frac{\Delta S_s^{\text{tr}}}{R} + \frac{{}_a G^{\text{vib}} - \frac{1}{2} N h \nu}{RT} - \frac{1}{2} - \ln \theta_s + \ln 760 \quad (56)$$

If the vibrations normal to the surface be taken as harmonic, then

$$\frac{{}_a G^{\text{vib}} - \frac{1}{2} N h \nu}{T} = \ln \left(1 - \exp \frac{N h \nu}{RT} \right) \quad (57)$$

The relations developed above are required for the analysis of adsorption data, and examples of how they are applied have been reported by Ross and Olivier (9,10). In these applications a number of properties of the adsorbate-adsorbent system are introduced as quantities in the mathematical description of the adsorption phenomenon; these are V_β and γ , descriptive of the adsorbent; α and β , descriptive of the adsorbate; and the modification of α , due to the interaction of adsorbate and adsorbent. In addition, the nature of the adsorbed phase determines the entropy change, the number of new vibrations peculiar to a molecule held at a surface, and the change of kinetic energy of the molecule on adsorption. All this information cannot be extracted from an interpretation or analysis of adsorption data alone, at least not definitively; whatever additional information can be brought in from other sources strengthens the authority by reducing the ambiguity of that interpretation. Among the sources of pertinent information are infrared absorption spectroscopy of the adsorbed molecules (11), nuclear magnetic resonance (12), diffraction of low energy electrons (13), and, though not yet applied because of existing technical difficulties, absorption spectroscopy in the microwave region.

The precise measurements reported by Halsey et al. in the Henry's law region of the adsorption isotherm can be interpreted by means of equations 58 and 56 but only

if reasonably accurate values of V_β and γ are already known for the adsorbent. Values of these quantities cannot be obtained from such measurements alone without additional hypotheses and assumptions. Fortunately, the adsorbent used, a graphitized carbon black, had already been distributed widely to different investigators, so that a body of additional data was available from which the values of the desired quantities could be elicited with assurance. One knew, for example, that this adsorbent possessed a high degree of surface uniformity, so that γ would be a large number (estimated $\gamma = 400$); hence the term in γ in equation 51 is small enough to be neglected. The equation then reduces to

$$\ln Z + \ln A^0 = (U_0/RT) + \ln V_\beta$$

(58)

The monolayer capacity of the adsorbent had also been independently measured, and so could be expressed as V_β for the different adsorbates used by Halsey et al. To solve equation 58 the unknown frequency ν , assumed to be invariant with temperature, is obtained by a series of trials of different values, until one is obtained that satisfies equation 58. Every trial value of ν gives a new set of values of $\ln A^0$ and therefore of $\ln Z + \ln A^0$, as a function of T . The correct solution has been obtained when the plot of $\ln Z + \ln A^0$ against $1/T$ turns out to be a straight line that intercepts the $(\ln Z + \ln A^0)$ axis at a point corresponding to $\ln V_\beta$; the slope of the line equals U_0/R . The results of such analyses, in terms of U_0 and ν , for a number of adsorbates on the same adsorbent are collected in Table 1.

Table 1. Adsorption Parameters of Adsorbates on Graphite

	Ne	Ar	Kr	Xe	H ₂	D ₂	CH ₄	CD ₄
β , Å ² /molecule	8.95	13.6	15.7	18.5	12.1	12.1	16.4	16.4
V_β , ml/g (STP)	5.82	3.83	3.32	2.82	4.31	4.31	3.17	3.17
U_0' , kcal/mole	0.681	2.066	2.754	3.654	0.956	1.032	2.678	2.644
$10^{-12} \nu$, sec ⁻¹	1.19	1.28	1.00	0.85	10	7	2.48	2.04
${}_oP^{\text{ads}}$, kcal/mole	0.737	2.12	2.80	3.69	1.436	1.366	2.796	2.741
${}_oP^{\text{elec}}$, kcal/mole	0.043	0.180	0.256	0.415	0.082	0.082	0.270	0.270
${}_oP^{\text{disp}}$, kcal/mole	0.694	1.94	2.54	3.28	1.354	1.284	2.526	2.471

The total interaction between adsorbate and adsorbent is measured by the depth of the potential well, or the maximum loss of potential energy on adsorption, as illustrated in Figure 4. The depth of the well, symbolized by ${}_oP^{\text{ads}}$, is given by equation 32,

$${}_oP^{\text{ads}} = U_0 + \frac{1}{2} N h \nu$$

values of ${}_oP^{\text{ads}}$ calculated from U_0' and ν are reported in Table 1. The depth of the potential well, representing the total interaction between adsorbate and adsorbent, is itself the result of two contributions; namely, the potential energy due to London-type dispersion forces between the adsorbate molecule and the atoms comprising the solid, and a potential due to polarization of the adsorbate by the electric field at the interface, or

$${}_oP^{\text{ads}} = {}_oP^{\text{disp}} + {}_oP^{\text{elec}}$$

(59)

The surface electric field is ascribed to the electric double layer at the solid surface, due to electrons of the solid projecting a short distance outside; the effect can produce a

field of sufficient magnitude to induce significant electric moments in adsorbed molecules. An oriented dipole in the electric field cannot be removed without work, and this work contributes to the adsorption potential of the surface. By simple electrostatic theory, ${}_sP^{\text{elec}}$ is related to the surface field F by the equation

$${}_sP^{\text{elec}} = \frac{1}{2} F \mu^{\text{ind}} \quad (60)$$

where μ^{ind} is the induced dipole of the adsorbed molecule. Physically adsorbed molecules on metal surfaces always seem to produce dipoles that have their positive poles pointing away from the surface, which might be understood as the result of the molecules penetrating to some extent into the electronic atmosphere above the surface.

The measurement of F can only be made indirectly by observing effects produced by the adsorbed film. For metals, measurements of surface potentials can lead to an estimation of F ; for finely divided solids we can only deduce the existence and magnitude of F by observation of secondary effects produced by the surface-induced dipoles of the adsorbate. Similar dipoles all oriented the same way will reduce the normal forces of intermolecular attraction between adsorbate molecules, because of the mutual electrical repulsion that is generated. The change from normal behavior (ie, that exhibited by the molecules in the gas state) can be observed, and used to evaluate the repulsion force, which in turn leads directly to a value for the strength of the surface electric field. For graphite the value obtained in this way is $F = 1.2 \times 10^5$ esu/cm². For the adsorbates mentioned in Table 1, the values of ${}_sP^{\text{elec}}$, calculated by equation 60 are reported in the table; values of ${}_sP^{\text{disp}}$, calculated by equation 59 are also reported.

Crowell and Steele (14) have calculated the interaction potential of methane with graphite, using empirically determined potential constants. The value they calculate, corresponding to our ${}_sP^{\text{disp}}$, is 2.560 kcal/mole; which is in good agreement with the value of 2.526 kcal/mole reported in Table 1, as obtained from the experimental data by means of the present theory.

The adsorption data that are discussed above refer only to the Henry's law portion of the adsorption isotherm. All adsorption isotherms, no matter what the substrate, will display a Henry's law portion (ie, linear through the origin) at sufficiently low pressures, although for substrates of great heterogeneity the pressures at which this condition prevails may be too low for the usual type of measuring instruments. The interpretation of such data can only be made when additional information is available, namely the degree of substrate heterogeneity and the specific monolayer capacity of the substrate. These facts are themselves only to be evaluated from adsorption isotherms that extend to much higher pressures. The conclusion we are brought to is that the type of analysis we have illustrated, although capable of yielding much information about the adsorption system, is possible only in exceptional conditions.

The next higher range of pressures brings the adsorption to surface concentrations at which the two-dimensional gas cannot be considered as ideal. A useful equation of state for a nonideal gas is van der Waals equation,

$$\left(\pi + \frac{\alpha}{\sigma^2} \right) (\sigma - \beta) = RT \quad (61)$$

where α and β are two-dimensional van der Waals constants that are related to the normal (ie, three-dimensional) van der Waals constants a and b by the equation

$$\alpha/\beta = a/2b \quad (62)$$

When equation 61 is transformed, by means of equation 16, into its corresponding adsorption isotherm equation, we get

$$p = K \frac{\theta}{1 - \theta} \exp \left(\frac{\theta}{1 - \theta} - \frac{2\alpha\theta}{RT\beta} \right) \quad (63)$$

where K has the same significance as the K discussed in equation 17. If we follow that discussion, substituting the nonideal gas description provided by equation 63 in place of the ideal gas described by equation 2 we would obtain the following in lieu of equations 41 and 42:

$$K = A^0 \exp (-U_0/RT) \quad (41)$$

where

$$\ln A^0 = - \frac{\Delta S_s^{\text{ads}}}{R} + \left(\frac{{}_aE^{\text{vib}} - \frac{1}{2} N h \nu}{RT} \right) - \frac{\Delta E^{\text{kin}}}{RT} - \ln \frac{\theta_s}{1 - \theta_s} + \ln 760 \quad (42a)$$

As a description of the adsorption isotherm, equation 63 has two advantages compared to the Langmuir equation: it allows for the mobility of the adsorbate and it takes into account the influence of the adsorbed molecules upon each other (adsorbate-adsorbate interaction). That for physical adsorption, at all temperatures save those close to absolute zero, the adsorbed molecules are mobile is now becoming increasingly evident; calculations from experimental data of the entropy change on adsorption indicate that one degree only of translational freedom is lost rather than the three degrees that would be lost if the adsorbed molecule were immobile on one spot. Even in chemisorption, where the molecules are localized, migration along the surface from one site to another has been demonstrated. Also, and again more emphatically for physical adsorption, the adsorbate-adsorbate interaction should not be neglected in constructing a reasonably accurate model of adsorption phenomena. Like the Langmuir equation, however, equation 63 is postulated on the substrate being energetically uniform throughout for adsorption. Even with this last limitation, equation 63 has practical utility. A few solids are known that have a surface that is close to uniform, eg, graphitized carbon black; for such substrates the physically adsorbed film cannot be described by the Langmuir equation, whereas equation 63 is a satisfactory description both above and below the two-dimensional critical temperature (15). Even without this evidence, which came later, and in the teeth of a general predilection for the Langmuir equation, de Boer had devoted the greater portion of his monograph to exploring the implications of the two-dimensional van der Waals equation applied to the adsorbed film (16). His calculations were a brilliant prognostication of experimental results subsequently obtained by Ross and his co-workers, Clark, Winkler, Pultz, Olivier, and Machin.

Toward the real problem, this work, both in theory and in experiment, is but the first step; it does not take us beyond the consideration of completely homotattic surfaces, which are actually unobtainable, or surfaces almost completely homotattic, which are actually of rare occurrence. The surface of each of the common solid materials that we encounter daily offers a distribution of adsorption potentials. We are, therefore, now faced with the problem of using equation 63 for the explicit solution of θ_i in equation 45

$$\theta = \frac{1}{n} \int_e^a \theta_i \exp [-\gamma (U_0 - U_0')^2] dU_0 \quad (45)$$

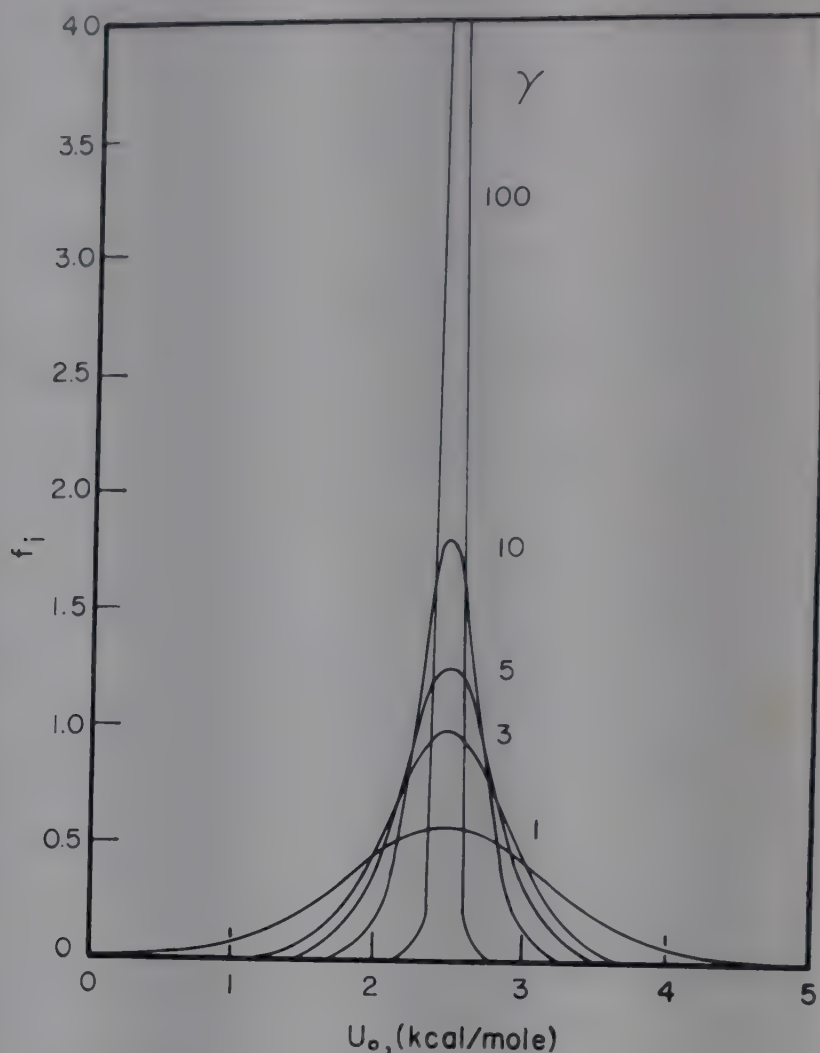


Fig. 5. Gaussian adsorptive energy distribution curves for several values of γ (eq. 44).

where θ_i is determined at any value of p by the equation

$$p = K_i \frac{\theta_i}{1 - \theta_i} \exp \left(\frac{\theta_i}{1 - \theta_i} - \frac{2\alpha\theta_i}{RT\beta} \right) \quad (63a)$$

Unfortunately equation 45 is an intractable integral, which can only be made useful by means of a computer. By this means, instead of an analytic expression for the adsorption isotherm, we obtain a series of computed isotherms for different values of the parameters. Although less convenient to use, these values can be obtained without the constraint of further mathematical restrictions that would otherwise modify the form or limit the usefulness of the functions in equation 45.

For use in the computer, equation 45 is treated as a summation of finite terms. The infinitesimal dU_0 becomes the finite interval ΔU_0 ; hence the infinitesimal fraction $d\delta_i$ in equation 43 becomes the finite interval $\Delta\delta_i$ with an adsorptive energy U_{0i} ; the whole surface is considered to be the sum of fifty homotattic patches. Equation 45 then becomes

$$\theta = \sum_{i=1}^{50} \Delta\delta_i \theta_i \quad (64)$$

To get the computed isotherm, each finite surface patch is treated as an individual homotattic surface of adsorptive energy U_{0i} for which the amount adsorbed, θ_i , at a pressure p , can be calculated by equation 63a using

$$K_i = A^0 \exp (-U_{0i}/RT)$$

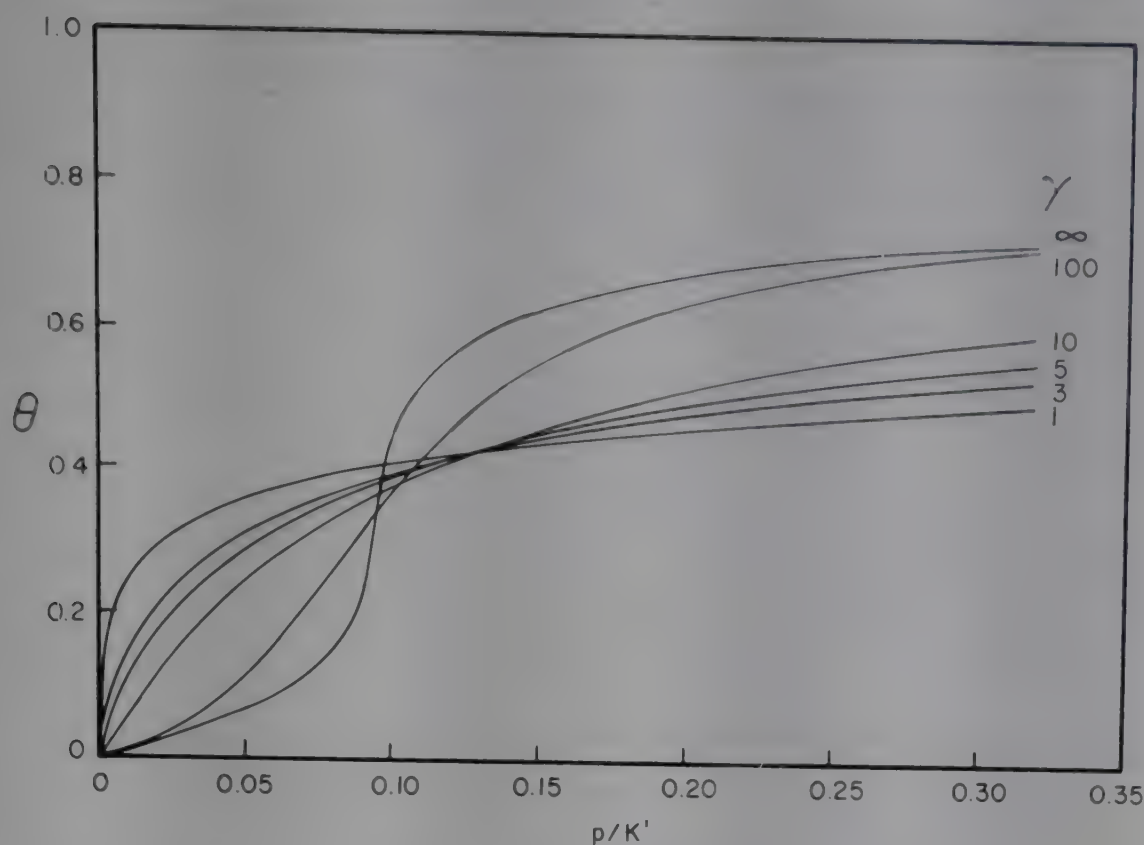


Fig. 6. Computed isotherms for argon adsorbed as a mobile film at 77.5 K, corresponding to the distribution curves shown in Figure 5.

where A^0 is defined by equation 42a. Figure 5 shows a number of Gaussian distributions of the adsorptive energy, calculated by equation 44 for several values of γ . Figure 6 shows a number of computed isotherms based on equations 45 and 63 ($2\alpha/RT\beta = 6.51$), corresponding to the distribution curves shown in Figure 5. The shape of these adsorption isotherms depends on the following parameters: V_β , which defines θ ; γ , which determines the width of the distribution curve; and K' , defined by

$$K' = A^0 \exp(-U'_0/RT) \quad (65)$$

where U'_0 fixes the location of the maximum of the distribution curve. The family of computed isotherms shown in Figure 6 varies in shape from the sigmoidal type that is characteristic of near-homotactic surfaces to the convex type usually associated with the Langmuir equation, but which now can be seen to arise as a possible description of a mobile adsorbed film on a heterogeneous surface. Almost any experimental adsorption isotherm can be expected to match one of these curves; the real test of the theory, therefore, is not so much the fitting of the data alone but also the reasonableness of the constants: (a) as determined by their ability to predict the variation of adsorption with temperature; (b) as revealed by the value of V_β , the monolayer capacity, compared with other estimates; and (c) as compared with other known characteristics of the surface.

The computed isotherms differ from experimentally obtained isotherms in that they record the variation of p/K' with θ rather than the experimentally observed p vs V . The purpose of matching experimental with the computed model isotherms is to obtain the appropriate values of K' , V_β and γ that will bring the experimental isotherm into coincidence with one of the model isotherms. The process of matching is purely one of trial and error, although by the adoption of simple graphical techniques much labor is avoided.

The first difficulty lies in the choice of an appropriate value of α/β in equation 63a. The surface field of the solid exerts an unknown influence on α . As a first approximation one can neglect this influence and use a value of α/β calculated from the normal van der Waals constants by equation 62. Where data are limited, eg, adsorption isotherms for only one or two temperatures, this is all that can be done; in many instances, it is all that need be done.

The computed model isotherms corresponding to the given value of $2\alpha/RT\beta$ chosen for the adsorbate and temperature used are plotted on a large sheet of rectangular coordinate paper as $\ln p/K'$ vs $\ln \theta$ for a series of γ values. The experimental isotherm is plotted on a separate sheet of paper as $\ln p$ vs $\ln V$. The two sheets of graph paper are superimposed so that the axes are parallel and the curve drawn through the experimental points is interpolated within the family of curves representing the model isotherms. The positioning of the experimentally determined curve is done by eye. The regularity and closeness of the points of intersection of the model isotherms near $\theta = 0.4$ is an additional aid to the proper positioning. One usually finds an unambiguous location for the experimentally determined curve; although with substrates of wide heterogeneity the $\ln p$ vs $\ln V$ curve is nearly a straight line (Freundlich equation, eq. 5), from which no amount of effort has yet elicited the value of V_β . The source of the difficulty in such cases is that the surface contains so much area of low adsorptive potential that second-layer adsorption occurs before the filling of the monolayer is made evident; in other words, adsorption on the second layer blends into and is indistinguishable from the completion of the monolayer on a low energy portion of the substrate. The effect can perhaps be avoided by measuring adsorption isotherms on such surfaces at temperatures well above the critical temperature of the adsorbate, so that second-layer formation is discouraged; very high pressures would of course be required to ensure that at least 70 to 80% of the surface was covered by the monolayer. The adsorption isotherm thus produced could then be matched in the normal way.

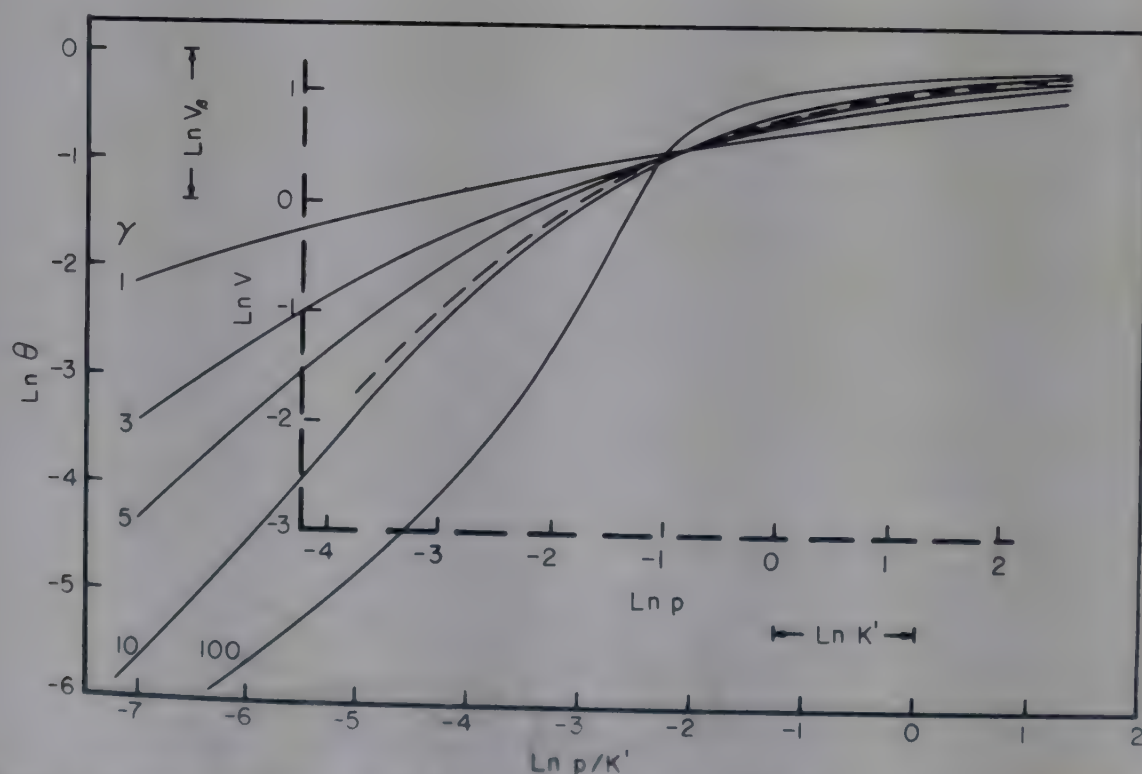


Fig. 7. Model isotherms (solid lines) and a superposed experimental isotherm (dashed line) in its proper interpolated position.

Figure 7 shows a number of the plots of the model isotherms and a superimposed experimentally determined isotherm in its proper interpolated position. The x - y displacement of the origin of the experimental graph relative to that of the graph of the models measures the scale factors that are required to bring the two sets of axes into coincidence. Thus the distance between the $\ln p$ axis and the $\ln p/K'$ axis, which is the displacement in the y direction of the two graphs, is equal to $\ln V_\beta$; similarly, the distance between the $\ln V$ axis and the $\ln \theta$ axis, which is the displacement in the x direction, is equal to $\ln K'$. The third parameter γ is obtained from the interpolated position of the experimental curve within the family of model isotherms. A number of adsorption systems that have been described by this method are reported by Ross and Olivier (9). The values of the constants obtained by this method describe the degree of heterogeneity of the substrate in terms of the distribution of its adsorption potentials and the average adsorption potential (U_0'); the monolayer capacity of the substrate for the adsorbate used is also evaluated (V_β). The surface electric field had been taken as negligible and so had not been evaluated; the adsorbed molecules had also been assumed to rotate as freely when held by the surface forces as they do in the gas state; finally, the vibration normal to the surface had been disregarded. Except for substrates of an extremely small degree of heterogeneity, which can without undue error be regarded as completely uniform, adsorption data alone cannot at the present time be analyzed to yield definitive information about surface electric field, orientation of the adsorbate, or vibrational frequencies of the molecules on the surface.

CHEMICAL ADSORPTION (CHEMISORPTION)

Physical adsorption takes place on all surfaces, though it is only sufficiently pronounced to be observed at temperatures lower than approximately half the critical temperature of the adsorbate. Chemical adsorption, on the other hand, is observed at temperatures either above the critical temperature of the adsorbate or such that the range of pressures involved is well below that required to saturate the surface with a close-packed monolayer. The high heats of chemical adsorption (40 to 100 kcal/mole) that are usually observed are the reason that adsorption takes place at all at such relatively high temperatures or low pressures. Chemical adsorption also requires a much higher temperature for the removal of the adsorbed gas than does physical adsorption, since E_d , the energy of activation of the desorption process, is equal to E_a , the energy of activation of adsorption, plus the heat of adsorption. The energy of activation is calculated from the times, t_1 and t_2 , required at temperatures T_1 and T_2 in $^\circ\text{K}$, to cause a given volume of gas to be adsorbed, according to the equation,

$$2.303 \log \frac{t_1}{t_2} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (66)$$

On iron the energy of activation of the adsorption process for nitrogen is about 16 kcal/mole, while for desorption it is about 51 kcal/mole (17). The rate of desorption is, therefore, very slow at temperatures below about 400°C . The large heats of chemical adsorption are due to specific solid-adsorbate interactions, which generally confine the amount adsorbed to a monolayer of adsorbate molecules bonded to localized sites on the substrate.

The Langmuir adsorption isotherm (eq. 10) is based on a model that more closely resembles the mechanism of chemical adsorption than that of physical adsorption,

and has indeed frequently proved satisfactory both as a description of the adsorption isotherms and of the uniformity of the heat of adsorption with surface concentration. Both descriptions should be observed experimentally before the Langmuir model can be considered satisfactory. The uniformity of the heat of chemical adsorption with surface concentration may result from two quite dissimilar causes. The adsorbate molecules may be able to react only with specific chemical configurations on the surface and so will select only these suitable sites, which are of course all uniform, and disregard the rest of the surface; or the *whole* heterogeneous surface may be significant for chemical adsorption, but the mobility of the adsorbed molecules be so low that the first portion of adsorbate to reach the surface takes up the most readily available sites, giving an integral heat of adsorption corresponding to an average of the distribution of adsorption energies. Succeeding portions of adsorbate take up other groups of sites, which have the same distribution of adsorption energies and so evolve the same average heat of adsorption. Since the uniformity of the heat of chemical adsorption with surface concentration can be achieved by these means, without having to introduce the improbable assumption that the whole substrate is homotactic, the Langmuir model is of far wider use and application in chemical adsorption than in physical adsorption.

Some experimentally observed examples of chemical adsorption cannot be described, however, without taking into account a surface distribution of the adsorption energies. For example, an exponential distribution function of the form

$$f_i = \Phi(U_0) = \frac{1}{n} \exp(-U_0/U_0') \quad (67)$$

gives for the adsorption isotherm equation,

$$\theta = \frac{1}{n} \int_0^\infty \theta_i \exp(-U_0/U_0') dU_0 \quad (68)$$

where θ_i is given by equation 10. On integrating this equation one obtains the Freundlich equation (eq. 5). Another type of distribution, suggested by Temkin, is to take

$$U_0 = C(1 - \alpha\theta) \quad (69)$$

In combination with the Langmuir equation this gives (approximately), for the adsorption isotherm,

$$\theta = \left(\frac{RT}{\alpha C} \right) \ln p + \text{constant} \quad (70)$$

Trapnell (18) gives the adsorption of nitrogen or of hydrogen on iron as examples of systems described by the Temkin equation.

These adsorption isotherms do not take into account the dissociation of the adsorbate molecule on the substrate. Many catalysts, for example, adsorb hydrogen by a dissociative chemisorption mechanism. The adsorbed hydrogen molecule, when dissociated into atoms, requires two adjacent sites on the surface; following Langmuir's model of adsorption, equations 6 and 7 now become

$$u = k_2 p [Z/(Z - \theta)] (1 - \theta)^2 \quad (71)$$

where Z denotes the number of nearest neighbor sites to a given site; for desorption,

$$v = k_1[(Z - 1)^2/Z(Z - \theta)] \theta^2 \tag{72}$$

The isotherm equation is then

$$\theta = (bp)^{1/2}/[1 + (bp)^{1/2}] \tag{73}$$

where

$$b = (k_2/k_1)[Z/(Z - 1)]^2 \tag{74}$$

This equation, due to Miller (19), has been used to describe the chemical adsorption of hydrogen by tungsten (20).

Lennard-Jones has demonstrated by means of potential curves how the energy of activation arises in such dissociative adsorption mechanisms (21). Figure 8 illustrates

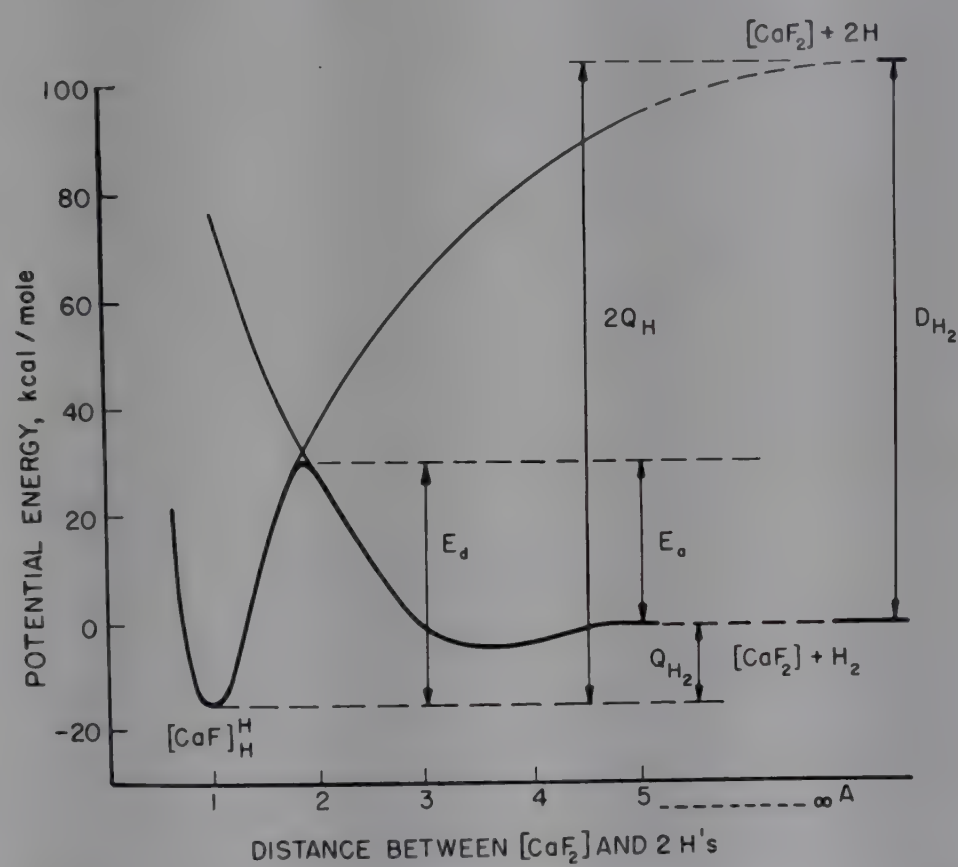


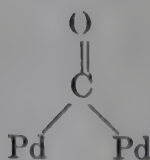
Fig. 8. Potential curves for the dissociative chemical adsorption of hydrogen on a calcium fluoride surface, after de Boer. Courtesy J. H. de Boer and Academic Press, Inc.

the chemical adsorption of hydrogen atoms on a CaF_2 film, whose surface is readily covered by a monolayer of atomic hydrogen (22). The curve, $[\text{CaF}_2] + \text{H}_2$, represents the variation of potential energy as the hydrogen molecule approaches the surface. The adsorption potential minimum of the physically adsorbed hydrogen molecule is shallow, with the relatively long equilibrium distance from the surface corresponding to the van der Waals radius of the molecule. The curve, $[\text{CaF}_2] + 2\text{H}$, represents the potential energy curve for the approach of two hydrogen atoms, which drop to a much deeper potential minimum corresponding to the chemical adsorption of the two atoms; these are at the relatively short distance from the surface corresponding to

the chemisorption bond. The diagram shows how a hydrogen molecule that has energy equal to or greater than the activation energy E_a may be able to approach the surface closely enough to cross over to the second curve. Once chemically adsorbed as atoms, the hydrogen is not appreciably desorbed at room temperature; from the rates of desorption at elevated temperatures an activated energy of desorption, E_d , of more than 40 kcal/mole may be estimated (eq. 66), which leads to a heat of adsorption of atomic hydrogen on CaF_2 , Q_H , of approximately 60 kcal/mole. Figure 8 shows that the dissociative chemical adsorption of molecular hydrogen on CaF_2 films is an exothermic process with a high energy of activation.

Although Figure 8 represents an exothermic adsorption reaction with a much larger heat of adsorption than is found for physical adsorption, de Boer has pointed out several examples where the chemical adsorption is endothermic (23). As chemical adsorption is essentially a chemical reaction between the adsorbed molecules and the outer layer of the adsorbent, and as endothermic chemical compounds are well known, an endothermic chemical adsorption is also possible. Physical adsorption, on the other hand, which is analogous to condensation of a vapor, is always exothermic. This consideration deprives us of the rule (save as a rough generalization) that we can distinguish chemical adsorption from physical adsorption by virtue of the much greater exothermic character of the former phenomenon. The only genuine criterion is the nature of the adsorptive bond. If the bond is due to van der Waals forces, electrostatic polarization, or electrical images, we call it physical adsorption; in chemisorption the bond is due to electron transfer, either partial or complete, between the adsorbate and the surface. The chemisorption interaction is conveniently discussed in terms of electronic band theory, which has been worked out most completely for metal surfaces. An ionic bond is formed, for example, when the ionization potential of the adsorbate is less than the work function of the metal; the valence electron of the adsorbed atom then transfers to the metal and a layer of *positively* charged ions is created on the surface. Alternatively, if a vacant energy level exists in the adsorbate below the Fermi level of the metal, an electron can transfer from the metal to the adsorbate, as happens when oxygen is chemisorbed on a metal surface in the form of *negative* ions. Covalent bonds are formed by electron exchange to create a bonding orbital, such as may arise from the interaction of an electron from a filled band of the metal and one from the adsorbate. For metal surfaces the changes of the work function caused by the presence of adsorbates can be studied by measuring surface potentials (24), but the interpretation of these measurements in terms of ionic or covalent adsorption has not yet been made definitive.

The infrared spectra of adsorbed molecules seem to offer at present the most satisfactory means of obtaining detailed information about the nature of the adsorptive bond. The infrared spectra of physically adsorbed molecules are similar to the spectra of the gaseous, liquid, or dissolved states. Minor differences in band positions may indeed be observed in physical adsorption, but they are of the same magnitude as the differences between the various unadsorbed states (gas, liquid, or solution of the adsorbate); no new bands are found that cannot be attributed to vibrations already known from infrared or Raman bands of the gaseous or liquid states. But for chemisorbed molecules the infrared spectra are markedly different from those of the unadsorbed states. Carbon monoxide, for example, chemisorbed on a supported palladium catalyst, produces hitherto unobserved bands in the $5.2\text{--}5.5\ \mu$ region, which are interpreted (25) as due to CO chemisorbed in the bridged structure.



The number of bands increases with the surface concentration of chemisorbed CO, which is attributed to the surface heterogeneity of the solid Pd; each band results from a separate homotactic patch, identified with each of the major crystal faces of the adsorbent. The infrared spectra can also distinguish two or more simultaneously occurring but different types of chemisorbed bond between the adsorbate and various parts of the surface. Both quantitative and qualitative differences in the nature of chemisorbed bonds can therefore be traced to structural differences in the lattice of the substrate.

Investigation of the catalytic activity of different faces of a crystal have been cited as evidence for the influence of lattice geometry on heterogeneous catalysis. Such interpretations must, however, be accepted with reservations. The rates of reaction between ethylene and hydrogen on evaporated films of the transition metals, as determined by Beeck and his associates (26), can be correlated with either the lattice spacing of the surface planes or with the percent *d*-electron character of the metal bond. Rhodium, with a spacing of 3.75 Å, has the greatest activity and also has the highest percent *d*-electron character. The question then arises if the hydrogenation of ethylene proceeds most readily on a rhodium substrate because of the favorable geometry provided by the 3.75 Å spacing or because of the high heat of adsorption resulting from the high *d*-electron character of the metal bond. To select the geometrical factor only as determining the forces at the surface of a solid is an oversimplification, although unquestionably large net differences exist between the action of one crystal face and another (27).

Adsorption from Solution by Solids

The adsorption of a solute, from its solution, by a solid surface is a phenomenon considerably more complex than that of the adsorption of a gas or vapor by a solid surface; the number of components in the adsorption system is now increased by one, so that we have at least a three-component system, and our knowledge of the liquid state is notoriously more limited than our knowledge of gases. As a first approximation, however, we can think of the phenomenon as a distribution of the solute, now known as the *adsorptive*, between the liquid solvent and the solid surface, both of which are competing for it.

Solid adsorbents are roughly classed as polar or nonpolar. On polar surfaces ion-dipole or dipole-dipole interactions with the adsorptive are more prominent than interactions due to dispersion forces; on nonpolar surfaces, the latter predominate. Examples of polar adsorbents are alumina, barium sulfate, calcium carbonate, glass, ion-exchange resins, quartz, silica gel, titanium dioxide and most metallic oxides, and zeolites; examples of nonpolar adsorbents are carbon blacks, charcoals, graphite, organic resins and plastics, paraffin, stibnite and most metallic sulfides, and talc. Both adsorptive and solvent molecules can also be classified in the same way. A polar molecule has a dipole moment, or a group, or even a bond, that is electrically dissymmetric; a nonpolar molecule lacks this feature. The competition for the adsorptive can be made to depend on polar versus nonpolar interactions. A polar ad-

sorptive will tend to prefer the more polar phase; a nonpolar adsorptive prefers the more nonpolar phase. Thus, for example, the order of increasing extent of adsorption of a series of different adsorptives on a silica surface is the reverse of that for the same adsorptives on sugar charcoal: ie, the more polar the adsorptive molecule the greater its adsorption potential for the polar silica surface, and the less its adsorption potential for the nonpolar charcoal. In general, the order of the extent of adsorption on silica will also hold for other polar adsorbents, and the order found for charcoal will hold for other nonpolar adsorbents. Water is readily adsorbed by and therefore "wets" polar surfaces, which for that reason are often called hydrophilic; whereas nonpolar surfaces are not "wetted" by water and are called hydrophobic.

Molecules that combine both polar and nonpolar groups in their constitution are most readily adsorbed out of solution since they can orient themselves at the interface with their polar portion toward the polar phase and their nonpolar portion toward the nonpolar phase. Among molecules of this type we find all surface-active agents; this kind of adsorption by such molecules in aqueous solution accounts for their wetting and detergent action (qv). The nonpolar portion of these molecules is usually an aliphatic hydrocarbon chain, whose nonpolar characteristics increase regularly with increasing chain length. Traube investigated the lowering of surface tension caused by an homologous series of fatty acid alcohols and found that for compounds of increasing chain length the concentrations required to produce the same lowering of the surface tension were reduced to about one third of the previous value each time the chain was increased by one $\text{—CH}_2\text{—}$ group. The surface-tension lowering is an indirect measurement of the concentration of adsorptive at the liquid-air interface, and it has proved possible to make similar experiments to those of Traube by substituting a liquid-solid interface and measuring directly the quantity of solute adsorbed. For many systems thus studied the same rule stated by Traube can be applied; the quantity of solute adsorbed from an aqueous solution by a nonpolar adsorbent increases geometrically (ie, by a constant factor) each time the chain length is increased by one $\text{—CH}_2\text{—}$ group. Nonaqueous solutions show an inverse relation of the same sort; a polar adsorbent in a nonpolar solvent takes out less solute, by a constant factor, each time the chain length is increased by one $\text{—CH}_2\text{—}$ group. Adsorbents of less pronounced nonpolar surface may adsorb solute molecules by other attraction mechanisms than dispersion forces, eg, by electrostatic forces acting on ionic or polar groups; the simple generalizations expressed by Traube's rule would not then be applicable. We find, for example with cationic surface-active agents, that the positive ionic charge of the surface-active ion can be adsorbed by polar surfaces, such as glass or quartz, whereby the nonpolar portion of the adsorptive makes the solid surface hydrophobic; at higher concentrations of solute a second layer of surface-active ion adsorbs with a reverse orientation, so that the surface becomes hydrophilic and positively charged. The second layer of adsorptive would agree with the mechanism of Traube's rule, but the first layer would not.

The foregoing generalizations of adsorption behavior have been summarized by Cassidy (28) in the following rules to guide the prediction of the relative extents of adsorption.

Rule 1. Greater adsorption to a surface will occur from that system which produces the greater lowering of interfacial tension. This rule follows from the Gibbs relation. The interfacial tension is a manifestation (in part) of the unlikeness of the two phases. The adsorptive, as a result of adsorption, tends to reduce this unlikeness

and to make the transition in properties at the interface less abrupt. A corollary of this rule is that a liquid which is highly adsorbed by a solid will show a low interfacial tension against the solid.

Rule 2. The extent of adsorption is usually greater from solvents in which the adsorptive is less soluble. A corollary to this rule is that for a given adsorptive the better solvent will make the better eluent. This rule can be expected to hold well, particularly in those cases in which the solvents being compared show about the same interfacial tension toward the adsorbent being used.

Rule 3. The more polar the substance the more extensive its adsorption at a polar surface, other things being equal. A corollary to this rule is that a polar substance will be better adsorbed from a nonpolar solvent than from a polar one.

Rule 4. The less polar a substance the more extensive its adsorption at a nonpolar interface, other things being equal. But the range of values observed is usually not so wide as that found with polar solids. This may be one reason why polar solids are more favored for adsorption separations (except special separations such as decolorization); they are available with a greater range of activity.

Rule 5. Extent of adsorption changes in a regular manner along an homologous series. This rule is implicit in the concept of homology. Taken with 3 and 4 above a corollary follows: since relative polarity decreases up an homologous series, extent of adsorption to nonpolar surfaces should increase up the series. This is a restatement of the Traube rule. Another corollary might be stated: since relative polarity decreases up an homologous series, extent of adsorption to polar surfaces should increase down the series. *Rule 2* would warn, however, that, since solubility usually decreases (with any solvent) with sufficiently great increase in molecular weight, this second corollary must be applied with discrimination.

THE SOLUTION ADSORPTION ISOTHERM

The Langmuir and Freundlich isotherm equations have been widely applied to adsorption from dilute solution. For this application these equations have the following forms, respectively,

$$x/m = abC/(1 + bC)$$

(75)

and

$$x/m = kC^n$$

(76)

where x is the amount of solute adsorbed by m grams of the adsorbent when present at the concentration C in the solution; a , b , k , and n are constants. In equation 75, a is a measure of the surface area of the solid, so that $x/m = a\theta$, and b is the reciprocal of the constant K of equation 17 discussed above, and so is related to the adsorption potential U_0 by the equation

$$b = b' \exp (U_0/RT)$$

(77)

In equation 76 the constants k and n are relative measures of the surface area of the solid and its adsorption potential; the value of n is usually between 0.1 and 0.5. The Langmuir equation is based on the model of a uniform surface, or at least assumes that the heat of adsorption does not vary with surface concentration; the Freundlich equation can be derived by assuming an exponential distribution of adsorption potential energies. In effect, as we have seen, the special models by which these equations

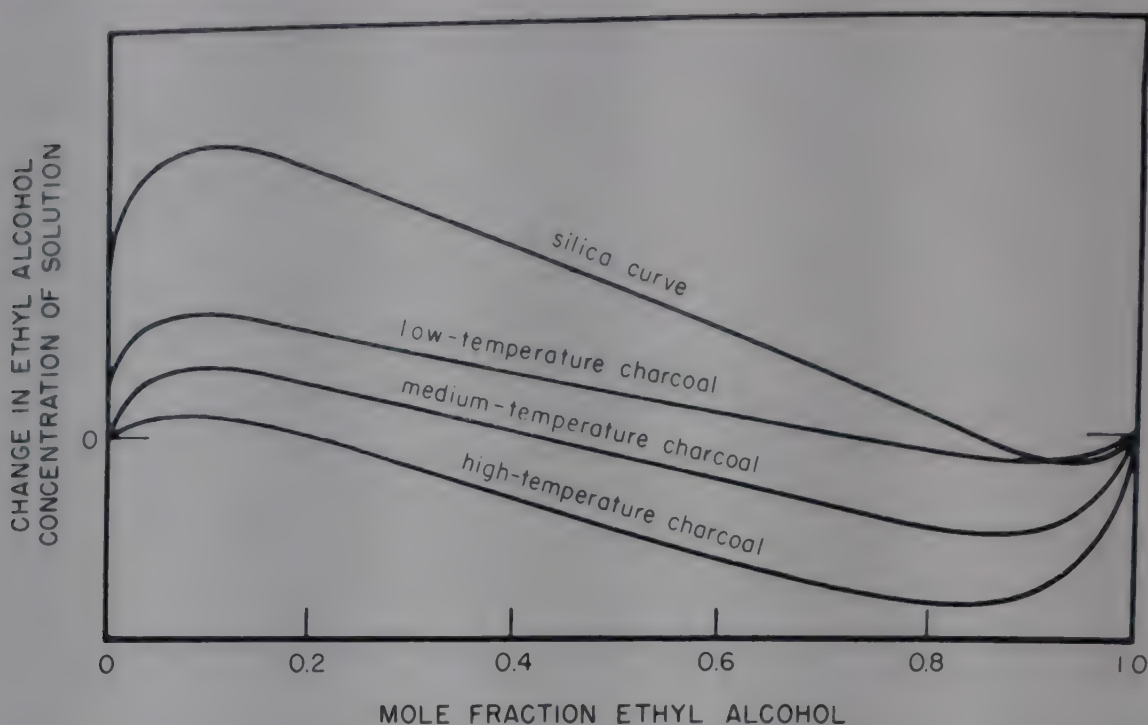


Fig. 9. Preferential adsorption of ethyl alcohol from benzene as function of charcoal treatment.

are derived cannot be proved to be valid even when the resulting equation describes the experimental data. These equations are therefore better regarded as empirical, unless additional information besides adsorption data is available about the system.

At higher concentrations these equations do not apply; frequently the adsorption of the solute appears to go through a maximum, then decreases and may become negative, as illustrated by the adsorption isotherms shown in Figure 9. For each adsorbent, ethyl alcohol is adsorbed from a benzene solution at low concentration; similarly, at low concentrations of benzene in ethyl alcohol, a preferential adsorption of benzene takes place, which also passes through a maximum. The peculiarity of a negative adsorption stems from the customary method of calculating the amount adsorbed, which is taken as proportional to the change in the concentration of solute in the solution as measured before and after adsorption has occurred. If the solution is found to be *more* concentrated after reaching equilibrium with the adsorbent, then the solvent rather than the solute has been preferentially adsorbed. When the simultaneous adsorption of the two components of the solution is taken into account the apparent anomaly of negative adsorption disappears.

Kipling and Tester have shown how the adsorption isotherm for the complete range of concentration, as shown in Figure 9, can be related to the vapor adsorption isotherms (29). They used the Langmuir equation to describe simultaneous adsorption from solution of the two components; they also assumed that the whole surface of the adsorbent was covered by the two adsorbed components, ie, $\theta_1 + \theta_2 = 1$. Under these conditions the fractions of the surface covered by each component are

$$\theta_1 = b_1 C_1 / (b_1 C_1 + b_2 C_2) \quad (78)$$

and

$$\theta_2 = b_2 C_2 / (b_1 C_1 + b_2 C_2) \quad (79)$$

The constants b_1 and b_2 in equations 78 and 79 can be derived from the vapor adsorption isotherms of the two components, which were measured by placing the adsorbent in the vapor phase of the solution; by analysis of the mixed adsorbate both (x_1/m) and

(x_2/m) were determined separately, even though mixed vapors were used. The vapor adsorption measurements provide an independent means of obtaining b_1 and b_2 for use in the mathematical description by means of equations 78 and 79 of adsorption from solution.

The heterogeneity of the adsorbent remains the unknown factor in all investigations of adsorption from solution. The presence of this factor nullifies all efforts to treat either the Langmuir or the Freundlich equations as anything more than empirical descriptions; different combinations of the solute adsorption mechanism and the distribution of adsorptive potential energies can lead to either of these equations, and to several other shapes of the adsorption isotherm besides. Recently Giles and co-workers (30) have attempted to classify solution adsorption isotherms for use in diagnosing adsorption mechanisms and measuring specific surface areas of solids. Their system of classification is based on the shape of the adsorption isotherm, and includes some of the shapes shown in Figure 6. These shapes are not peculiar to *mobile* adsorbed films: an almost identical series can be obtained by combining the Gaussian distribution of surface heterogeneities with an adsorption equation derived by Fowler and Guggenheim for a *localized* film with horizontal interactions (4). The shape of the adsorption isotherm, in short, is determined by an unknown combination of both horizontal interactions and surface heterogeneity, and whatever the one lacks in describing the data can be supplied by the other. The system of Giles et al. is, in effect, to equate the heterogeneity to zero and to interpret all differences as due to variations in the adsorption mechanism. The system will therefore be successful with near-homotattic surfaces but could be completely wrong for surfaces with a wide distribution of adsorption potentials. The latter type of surface, unfortunately, is by far the more common. The system of Giles et al. can, however, be applied with more probability of obtaining valid answers to the class of adsorption isotherms pertaining to the adsorption of dyes and other large molecules.

ADSORPTION OF DYES

The effect of surface heterogeneity can be suppressed by using adsorbates of large molecular size. This circumstance is perhaps the basis of the validity of dye adsorption as a technique for determining specific surface areas of solid adsorbents. The adsorption isotherm is always determined in the dilute range of concentrations where competitive adsorption of the solvent is not significant; such isotherms frequently show a saturation plateau at high equilibrium concentrations of the free dye. Sheppard and his co-workers (31), who investigated the adsorption of cyanine dyes by silver halides in connection with the study of optically sensitized photographic emulsions, concluded that the saturation plateaus observed in the adsorption isotherms of a number of cyanines adsorbed by silver bromide microcrystals corresponded to the formation of a close-packed monolayer of essentially planar cations, oriented with the planes of the molecules steeply inclined to the substrate, ie, a configuration in which the edge of the molecule is presented to the substrate (edge-on adsorption).

When the dye molecule is nonplanar or has a relatively high solubility in water, these being two distinct factors that reduce adsorptivity from aqueous solution, the type of isotherm shown in Figure 10, curve 2, frequently results (32). This isotherm shows the poor adsorptivity of the tetramethyl dye (curve 2 in the diagram) compared with its planar counterpart (curve 1), and curves 3 and 4 show the poor adsorptivity of 2,2'-cyanines whose molecules have been forced from planarity by bulky substituents

in the methine bridge. The discontinuity exhibited in the adsorption isotherm of the tetramethyl dye is accompanied by a change in the absorption spectrum of the adsorbed dye. In the low-concentration "foot" of the isotherm, the spectrum is that of the isolated molecule as modified by its adsorption, and probably corresponds to unassociated molecules in flat orientation with respect to the crystal surface; in the other region, the absorption maximum undergoes a bathochromic shift to a wavelength (*J*-band) similar to that of the oriented aggregates of planar dyes in solution (micelles). For the nonplanar dye, if the adsorption plateau is identified with the completion of a monolayer, the area per molecule is found to be consistent only with edge-on adsorption, although the average intermolecular distance, 5.98 Å, is greater

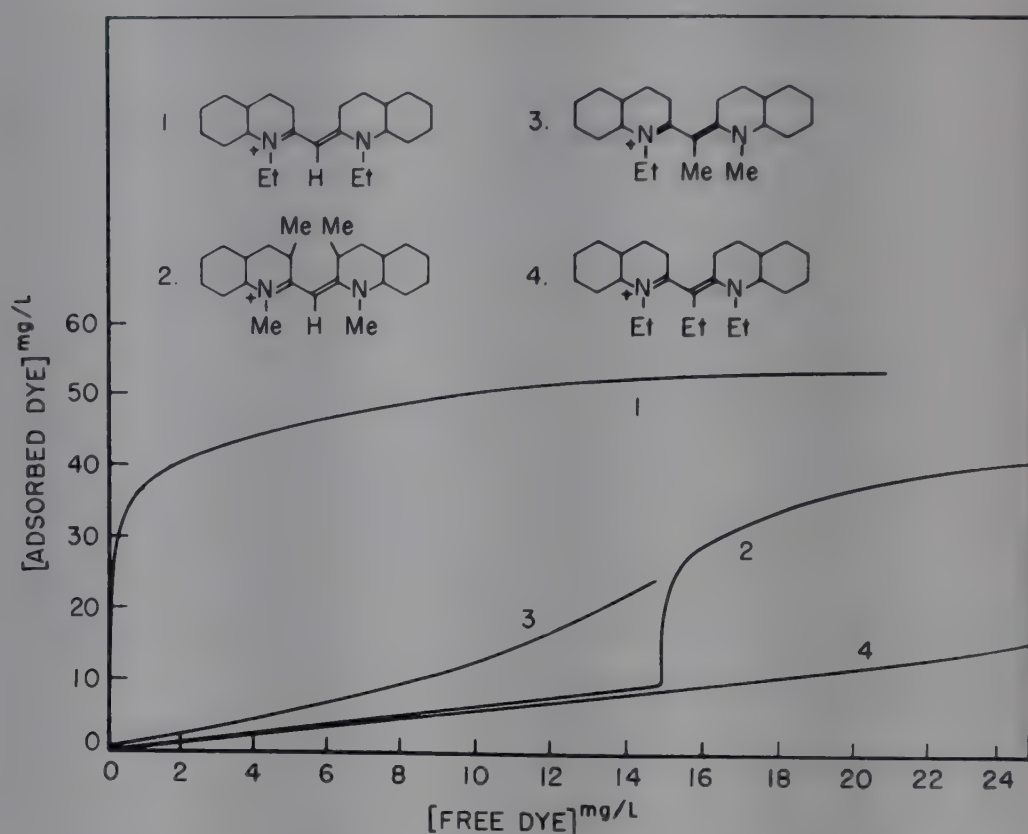


Fig. 10. Adsorption isotherms of cyanine dyes on silver bromide, showing the effect of nonplanarity of the adsorbate molecule. Courtesy W. West, B. H. Carroll, D. L. Whitcomb, and New York Academy of Sciences.

than for the corresponding planar molecules, as might be expected from the twisted configuration of the molecule.

For dyes such as 1,1'-diethyl-2,2'-cyanine, whose adsorption isotherm is shown in Figure 10, curve 1, the critical concentration at which lateral interactions become strong enough to induce cooperative edge-on orientation occurs in such a dilute solution that the isotherm appears to be continuous on the scale shown. Nevertheless a small foot, corresponding to noncooperative adsorption, can sometimes be found in the adsorption isotherm of well-adsorbed dyes; the effect can be magnified by making the adsorption conditions less favorable, eg, by introducing competing adsorbate or an unfavorable silver-ion concentration.

With systems such as these, the large size of the adsorbate molecule so masks the smaller scale heterogeneity of the substrate that conclusions about adsorption mechanisms drawn from the shapes of the isotherms have more validity.

Nomenclature

- A^0 = constant in equation 42
- C = number of components in system (eq. 1)
- C = constant in B-E-T Theory (eq. 11)
- ${}_aE^{\text{kin}}$ = kinetic energy of translation and rotation of an adsorbed molecule
- ${}_aE^{\text{rot}}$ = kinetic energy of rotation of a molecule in the adsorbed film
- ${}_aE^{\text{vib}}$ = average vibrational energy of an adsorbed molecule at temperature T
- ${}_aE_0^{\text{vib}}$ = average vibrational energy of an adsorbed molecule at 0°K
- ${}_oE$ = energy per mole, kinetic and potential, of a molecule in the surface film at infinite dilution
- ${}_oE^{\text{kin}}$ = total kinetic energy per mole of a molecule in the gas phase; for an ideal monatomic gas
 ${}_oE^{\text{kin}} = \frac{3}{2}RT$
- ${}_oE^{\text{rot}}$ = kinetic energy of rotation of a molecule in the gas phase
- ${}_oE^{\text{tr}}$ = kinetic energy of translation of a molecule in the gas phase
- ${}_oE$ = total energy per mole, kinetic and potential, of a molecule in the gas phase, at infinite dilution
- ΔE^{kin} = ${}_aE^{\text{kin}} - {}_oE^{\text{kin}}$
- ΔE^{rot} = ${}_aE^{\text{rot}} - {}_oE^{\text{rot}}$
- ΔE^{tr} = ${}_aE^{\text{tr}} - {}_oE^{\text{tr}}$
- F = number of degrees of freedom in system (eq. 1)
- F = surface electric field
- ${}_aG^{\text{vib}}$ = additional Gibbs free energy of the adsorbed phase due to molecular vibrations with respect to the surface (eq. 57)
- ΔG_s^{ads} = standard change in Gibbs free energy on adsorption
- ΔH_s^{ads} = standard change in enthalpy on adsorption
- K = constant in adsorption isotherm equation (eq. 25)
- K_i = particular value of K for the i th patch of a heterogeneous surface
- K' = particular value of K for the most frequent patch of a heterogeneous surface
- P = number of phases in system (eq. 1)
- P = energy barrier to desorption
- ${}_oP^{\text{ads}}$ = adsorptive potential between a gas molecule and the surface of an adsorbent at equilibrium separation (eq. 32)
- ${}_oP^{\text{disp}}$ = that part of ${}_oP^{\text{ads}}$ due to dispersion forces (eq. 59)
- ${}_oP^{\text{elec}}$ = that part of ${}_oP^{\text{ads}}$ due to interaction with surface electric field (eq. 60)
- ${}_aS$ = entropy of adsorbed phase
- ${}_aS^{\text{vib}}$ = additional entropy of the adsorbed phase due to vibrations with respect to the surface
- ${}_aS_s^{\text{tr}}$ = translational entropy per mole of the adsorbed phase in its standard state (eq. 55)
- ${}_oS_s^{\text{tr}}$ = translational entropy per mole of a gas in its standard state (eq. 55)
- ΔS_s^{ads} = standard change of entropy on adsorption (eq. 53)
- ΔS_s^{tr} = ${}_aS_s^{\text{tr}} - {}_oS_s^{\text{tr}}$
- U_0 = adsorptive potential of a homotattic surface (eq. 32)
- U_{0i} = adsorptive potential of the i th patch of a heterogeneous surface
- U_0' = adsorptive potential of the average patch of a heterogeneous surface
- V = amount adsorbed per gram of adsorbent, cc/g at STP
- V_m = amount adsorbed per gram of adsorbent when surface is saturated
- V_β = amount adsorbed per gram of adsorbent when area per molecule equals β
- Z = initial slope of an adsorption isotherm (eq. 50)
- a = van der Waals constant of a nonideal gas
- b = van der Waals constant of a nonideal gas
- f_1 = fraction of molecules striking a surface that remain long enough to change their kinetic energy (eq. 6)
- f_i = frequency of particular surface patches per unit energy interval
- i = number of interfaces to be considered in a system (eq. 1)
- m = mass of adsorbent
- n = normalizing factor in the Gaussian distribution (eq. 44)
- p = equilibrium pressure in a system
- p_0 = vapor pressure of the adsorbate
- p_s = equilibrium pressure corresponding to two-dimensional standard state (eq. 18)

- q^{diff} = differential heat (liberated) of adsorption
 q^{st} = isotheric heat of adsorption (eq. 22)
 q_s^{diff} = standard differential heat (liberated) of adsorption
 q_s^{st} = standard isotheric heat of adsorption
 u = rate of adsorption, molecules/cm²/sec (eq. 6)
 v = rate of desorption, molecules/cm²/sec (eq. 7)
 x = amount adsorbed in grams
 Γ = equilibrium surface concentration of adsorbate in moles/cm² (eq. 3)
 Σ = specific surface area of adsorbent, cm²/g
 α = two-dimensional van der Waals constant, corresponding to a (the same symbol is used for both molar and molecular quantities)
 β = two-dimensional van der Waals constant, corresponding to b (the same symbol is used for both molar and molecular quantities)
 γ = heterogeneity parameter in equation 44
 δ_i = $d\delta_i$ is the fraction of surface having energies between U_{0i} and $U_{0i} + dU_0$ (eq. 44)
 θ = fraction of the whole surface of adsorbent covered by an adsorbed layer of which each molecule has an area β , hence, $\theta = \beta/\sigma$ (eq. 13)
 θ_i = fraction of the i th patch of the adsorbent surface covered by the adsorbate (eqs. 46 and 63)
 θ_s = fraction of surface covered at the standard state of the adsorbed phase (eq. 24)
 μ^{ind} = dipole moment induced by the surface electric field (eq. 60)
 ν = vibrational frequency with respect to the surface acquired by a molecule on adsorption (eq. 57)
 ξ = electron polarizability of a molecule
 π = two-dimensional spreading pressure in dynes/cm (eq. 2)
 π_s = two-dimensional spreading pressure defining the standard state of the adsorbed phase ($\pi_s = 0.338$ dynes/cm) (eq. 24)
 σ = area per molecule (eq. 2)
 σ_0 = area per molecule at infinite compression (see also β)
 σ_s = area per molecule in the standard state of the adsorbed phase (eq. 24)

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ADSORPTION, INDUSTRIAL

When the solid-fluid contacting operation of adsorption is used to treat a fluid stream on an industrial scale, one of the following characteristics has usually been responsible for its selection as the most economic method for the treatment: high selectivity of the adsorbent; high concentrating power of the adsorbent, related to the selectivity; chemical instability of the adsorptive (solute), restricting it to temperatures unsuited for other separations; or fluctuating, or intermittent, supply of the fluid feed. See also Chromatography; Ion exchange; Molecular sieves; Separation methods.

Uses and Materials

The major economic uses of adsorption indicate the wide-spread applicability of the method and also suggest the areas in which new uses are most likely to develop. For *liquid-phase* treatment, the following types of process predominate:

- a. Decolorizing, drying, or degumming of petroleum fractions (solvents, fuels, lubricants, waxes).
- b. Odor, taste, and color removal from municipal water supplies.
- c. Decolorizing of vegetable and animal oils.
- d. Decolorizing of crude sugar syrups.
- e. "Clarification" of beverages and pharmaceutical preparations.
- f. Recovery of vitamins and other products from fermentation mixtures.
- g. Purification of process effluents for control of water pollution (includes ion exchange).
- h. Removal of salts or "ash" from process streams (includes demineralization by ion exchange, ion retardation, ion exclusion).

The primary *gas-phase* applications include the following:

- i. Solvent recovery from air leaving a chamber where an evaporative process, such as paint drying, newspaper printing, textile drycleaning, or rayon spinning, occurs.
- j. Dehydration of gases (including in-package desiccation).
- k. Odor removal and toxic gas removal in ventilating systems or from vent gases for air-pollution control.
- l. Separation of rare gases (krypton, xenon) at low temperatures.
- m. Impurity removal from air feed to low-temperature fractionation.
- n. Odor removal from municipal illuminating-gas supplies.

Other processes, where workability has been demonstrated but general large-scale use has not yet been reached, include the following:

- o. Liquid-phase separation of aromatic from paraffinic hydrocarbons in the same boiling-point range, as an alternative to extractive distillation.
- p. Gas-phase separation of low-molecular-weight hydrocarbon gases, alternative to rectified adsorption or to low-temperature distillation.

Table 1. Major Types of Adsorbents

Composition	Internal porosity, %	External void-fraction, %	Bulk dry density, lb/ft ³	Surface area, m ² /g	Uses ^a
acid-treated clay	~30	~40	35-55	100-300	a
activated alumina and bauxite aluminosilicate	30-40	40-50	45-55	200-300	a, i, j
"sieves"	45-55	~35	41-44	600-700	a, j, n, p
bone char	50-55	18-20	40	~100	d, h
carbons	55-75	35-40	10-30	600-1400	nearly all
fuller's earth	50-55	~40	30-40	130-250	a, c
iron oxide	22	37	90	20	n
magnesia	~75	~45	~25	200	a
silica gel	~70	~40	~25	~320	i, j, k, m

^a For explanation of symbols see list of uses a-p under Uses and Materials.

The major processes, together with the adsorbents used in them, have been reviewed extensively by Mantell (18) and less fully, for gas-phase treating, by Kohl and Riesenfeld (15). A comprehensive bibliography of adsorbent properties and uses has been assembled by Deitz (6).

Physical properties for the primary classes of adsorbent materials are listed in Table 1, along with the uses for which each material is particularly suitable. These uses are indexed according to the foregoing list.

Process Arrangement

Two major classes of treatment are encountered in adsorption; those in which the fluid and adsorbent follow identical paths through the process with equal residence times and without any segregation occurring between the two phases; and those in which segregation of fluid and adsorbent occurs to an appreciable extent.

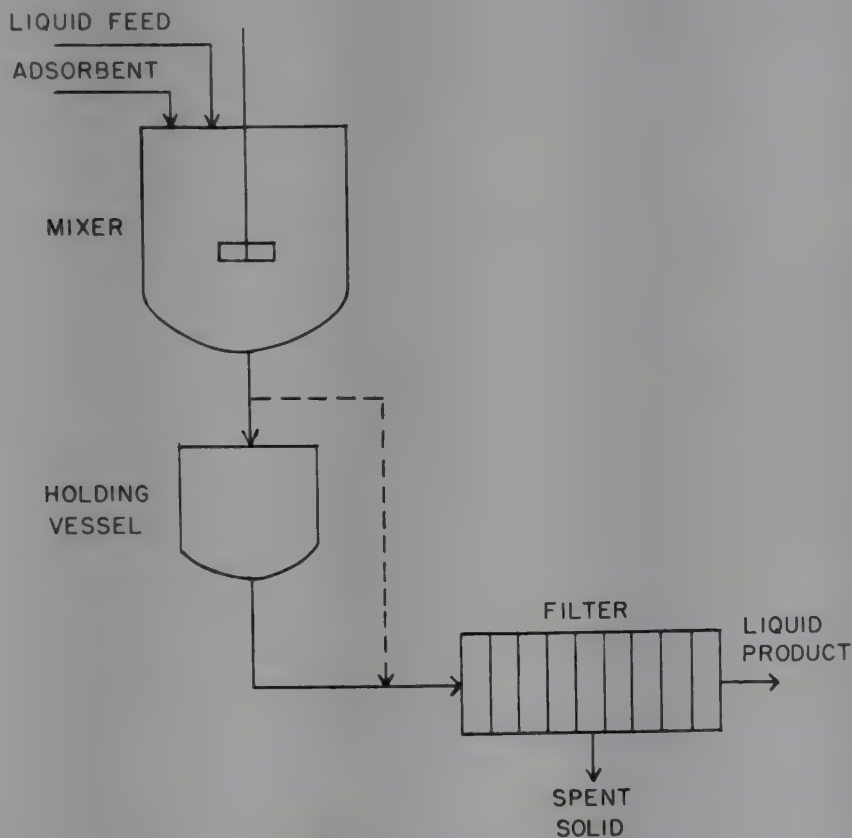


Fig. 1. Contact filtration.

Unsegregated movement of the two phases, between the point of mixing and the point where the mixture is filtered, is known as *contact filtration*. It can be carried on either in batch or as a continuous cocurrent operation. Figure 1 shows the process flow schematically, including an optional holding tank which would not be used in batch treatment. Nearly unsegregated treatment of a gas is shown in Figure 2, which illustrates pneumatic transport or light-phase fluidization as studied by Morita in connection with the Fluid-Char process for separation of hydrocarbon gases (20); in this case the gas-solid separation is effected in a cyclone.

Segregation of flows characterizes two different types of contactors. The counter-current-flow type is exemplified by the Hypersorption (12) and Fluid-Char (7) processes; a flow diagram for the former, illustrating the separation of ethylene (as bottom product) from methane (overhead), is given in Figure 3. The fractionating column

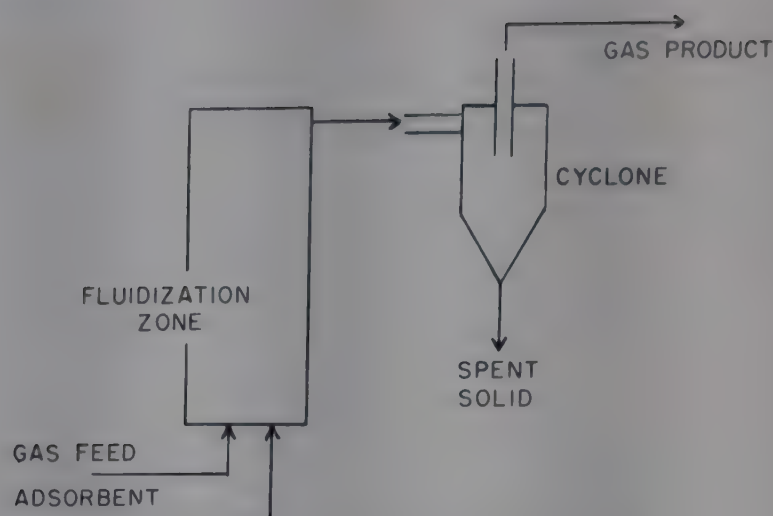


Fig. 2. Cocurrent gas-solid contacting.

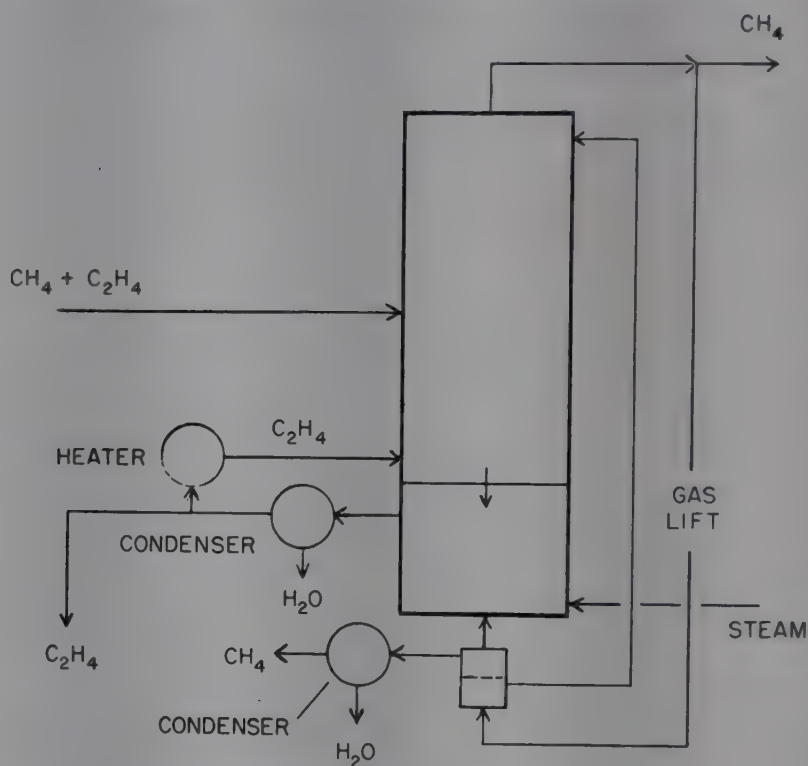


Fig. 3. Countercurrent adsorption.

proper is situated above a steam-stripping column in the same housing. The feed enters near the center of the fractionator and rises. Ethylene and some methane are adsorbed from the remaining methane before it reaches the top. A reflux of ethylene is fed at the bottom; this strips methane off the adsorbent in the lower part of the fractionator. The steam stripper then removes ethylene from the adsorbent; moisture is then removed from the solid by cooling it with a portion of the methane product. Granular activated carbon of 12–30 mesh is used in Hypersorption, while 50–100 mesh material is suitable for the Fluid-Char process.

The other type of segregated operation, which is semicontinuous, involves the use of fixed beds of granular adsorbent or, in some instances, *fluidized fixed beds* where the solid phase is held in the contactor but in a condition of nearly perfect mixing (see Fluidization). The frequent preference for fixed beds is easily understood. Moving a solid involves mechanical or manual operations that are expensive. The solid also incurs a greater risk of attrition and contamination than when all operations are performed by transporting the needed fluids to a stationary location for the solid.

In fixed-bed operation when the adsorbent in a given column has been used to capacity, flow must be discontinued while the solid is being regenerated or replaced. Continuous feed can be accommodated if two or more contactors are provided, with at least one in use at all times. In those cases where regeneration is rapid and a relatively long column is needed for complete purification, the inventory of solid can be reduced by using a cyclic arrangement in which one column after another can be removed from the processing step for regeneration and then returned to it. This arrangement is shown for three units in Figure 4 with A and B initially in the processing step and C in regeneration. Subsequently, A can be withdrawn for regeneration while feed passes through B and C in turn. Next, B will be withdrawn while feed passes through C and A and, finally, the initial conditions are again reached.

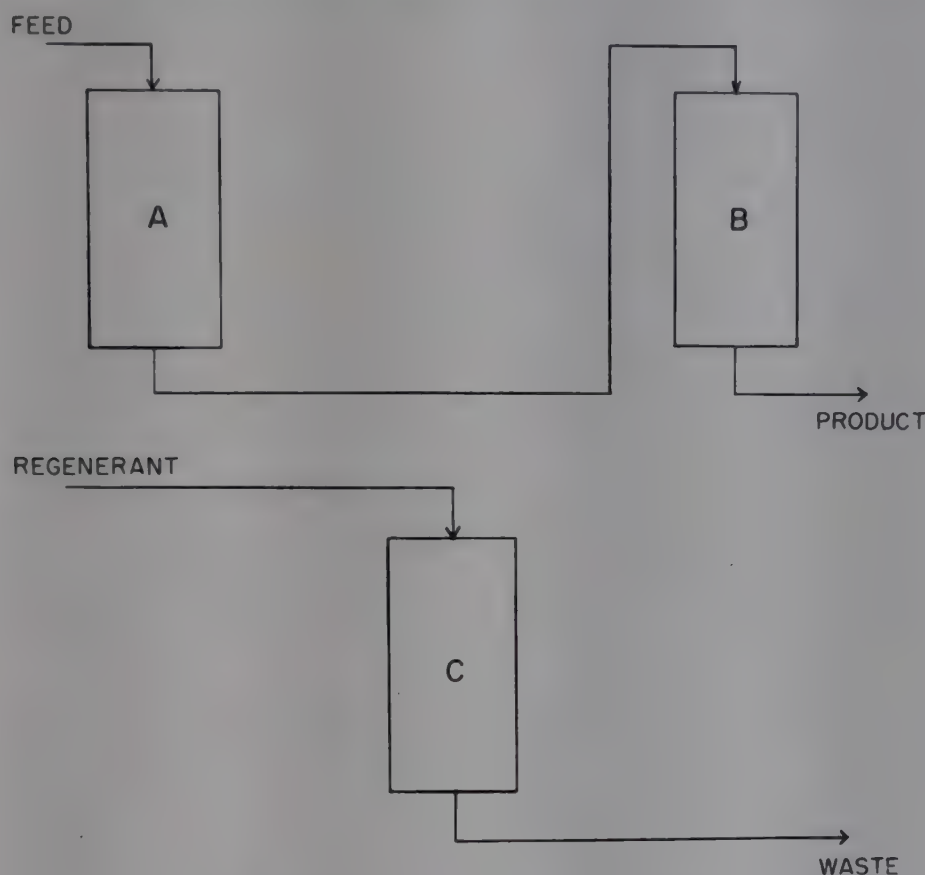


Fig. 4. Cyclic operation of fixed beds.

When the adsorbent requires more extreme *activation* or *renewal* treatment than is possible in the operating column (in particular a high-temperature, controlled-oxidation treatment), it may be transferred to a suitable furnace. Rotary kilns, gravity-drop burners, multiple-hearth furnaces, and the Thermoform kiln are used for this purpose (18). Cyclic operation of series of columns or beds may closely simulate the behavior of truly countercurrent systems.

Performance of Fixed-Bed Contactors

The separating behavior of an adsorbent in a fixed bed will now be examined in detail. This description applies rather generally to all fixed-bed operations, including ion exchange, leaching, drying of solids, regenerative heat transfer, and (with some elaboration) to all chromatographic separation, as well as to adsorption per se.

Fluid, either gas or liquid, enters the bed at a flow rate determined both by the allowable pressure drop within the bed and by the residence time needed to give es-

essentially complete removal of solute for a large part of the entire cycle. Generally, the solute is removed rather completely by the solid which it first contacts; the solute-free fluid then continues through the bed and out, nearly in equilibrium with the solid in the downstream part of the bed.

As the flow continues, the incoming fluid tends to reach equilibrium with the solid at the head of the bed and must then penetrate more deeply into the bed before discharging its load of solute. The boundary region between solute-saturated solid upstream and solute-free solid downstream has been termed the *adsorption wave* by Klotz (14) and others. This region, or wave, advances through the column as the fluid continues to flow; the ratio of its velocity to that of the fluid is the same as the volumetric distribution ratio of solute between the fluid and the adsorbent. When the adsorption wave approaches or reaches the downstream end of the column, flow of the feed fluid must be interrupted, and steps must be taken (also by a flow process) to regenerate the adsorbent in the column.

The accumulation of solute in the column for a linear isotherm is shown schematically in Figure 5. The abscissa, X , is proportional to the height of the column, and the contours represent successive times during the passage of fluid at a uniform flow rate. The ordinate, Y , is in dimensionless concentration or partial-pressure units. The *relative bed length*, N , is a theoretical parameter, equal to the number of mass transfer units for the column; it increases with the mass transfer rate and the actual column height and varies inversely as the flow rate. The *relative time*, NZ , is measured on a scale proportional to the relative bed length. For large values of relative bed length (values of 20–100 are fairly common), the contours take on an S shape that centers on the abscissa value equal to the relative time. For example, with $NZ = 10$ and also $N = 10$, the relative concentration, Y , is 0.46. At higher values of the relative bed length, each with the relative time equal to it, the ordinate value approaches progressively closer to 0.50.

As the relative bed length increases, the efficiency of utilization of the adsorbent improves in any one cycle of operation. Suppose, for instance, that no more than 10 percent of the feed level of solute can be tolerated in the outflow from the column; this is equivalent to $Y = 0.10$ (or actually, slightly less). For a relative bed length of 5, this value of Y is reached in a relative time of 2.2 units which represents 44 percent of the theoretical maximum utilization of the bed. For a relative bed length of 10, the concentration limit is reached in a relative time of 5.5, which is equivalent to 55 percent utilization.

Figure 5 refers not only to the total length of the column but also to any fractional length. If a relative bed length of 5 is equivalent to a true height of 5 feet, and if a relative time of 5 corresponds to an actual 5 hours, then Figure 5 gives the relative concentration on the solid at a depth of, say, 1.5 feet for times equal to 0.5 hour, 1.0 hour, or other times between or beyond these values. Since the bed of interest has a value of $N = 5$ at its outlet end, only that part of the plot to the left of $N = 5$ is significant for this particular case; the contours to the right of this abscissa become entirely fictitious. Whether or not the column extends further downstream has no appreciable effect at any point upstream. If our 5-foot column is supplemented by a second 5-foot column of like cross-sectional area with the flow rate and adsorbent composition remaining unchanged and the entire system starting in solute-free condition at zero time, the concentration profiles in the newly added column will be given by points that lie between $N = 5$ and $N = 10$ in Figure 5.

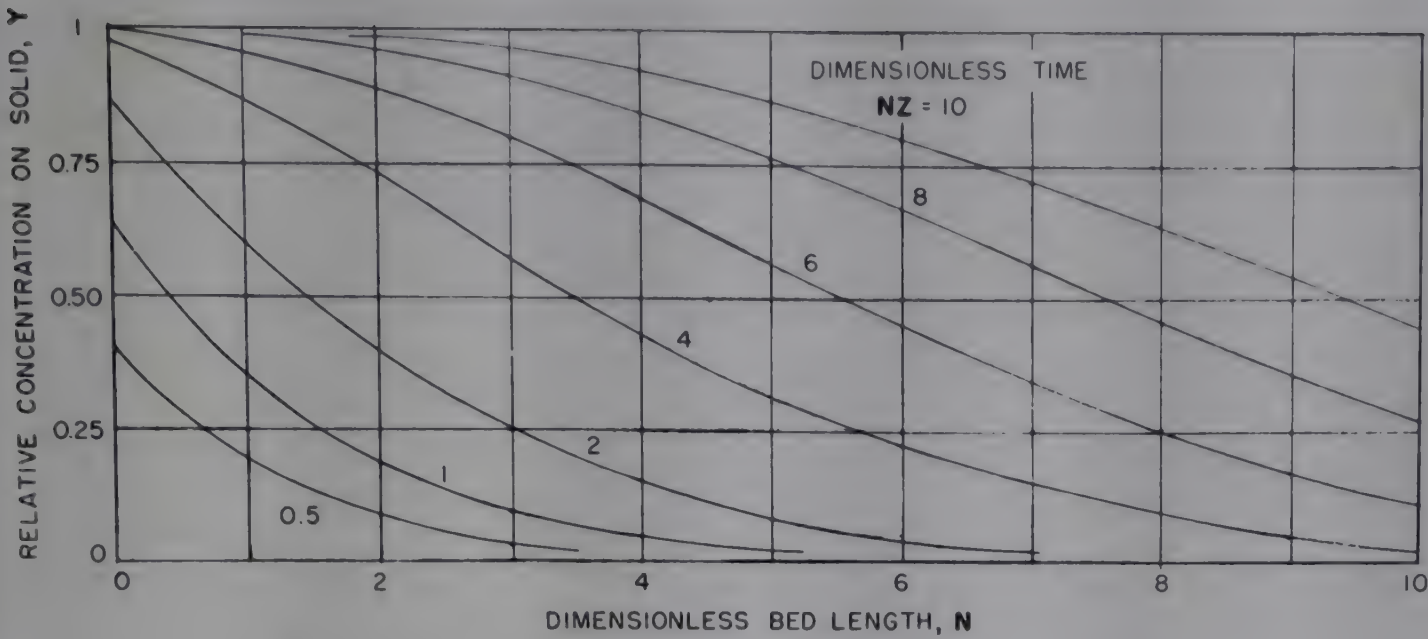


Fig. 5. Concentration profiles in the adsorbent (linear isotherm).

Although it is easier to describe the behavior of an adsorption column in terms of solid or fluid concentration levels within the column, the behavior of the outflow concentration is of much greater practical interest. For relative bed lengths of 40 or more, the relative solid concentration, Y , and fluid concentration, X , values agree within 4 percent in the linear isotherm case; hence the X values might be estimated from an extension of Figure 5 into the higher N region. The curves of concentration against time, at constant bed length, are called concentration histories, breakthrough curves, or leakage plots. Such curves start with the concentration close to zero and continue almost horizontally in that region until the value of NZ begins to approach that of N , whereupon the X curve rises (more or less steeply) toward 100 percent and then levels off again. Concentration values in this latter range correspond to the condition in which the column is so saturated that the feed fluid remains entirely unchanged upon passing through it. When plotted on linear coordinates, the breakthrough curves have an S shape which is almost the mirror image, from right to left or from top to bottom, of the curves in Figure 5.

Figure 6 shows the generalized breakthrough curves, still for a linear isotherm, on another system of coordinates. The probability scale taken as ordinate expands the regions in the vicinity of 0 and 1 and thus converts the S-shaped curves to a nearly linear form. The logarithmic scale for the abscissa makes it possible to plot experimental data on a true time scale and to compare the data to the theoretical curves by lining up the ordinates of the theoretical and experimental plots (on the same scale) and sliding the abscissas past one another until the theoretical curve that best fits the experimental run is found. The abscissa of Figure 6 uses a different relative time scale than does Figure 5. In Figure 6, NZ has been divided by N to yield a Z scale that centers about the value of 1.0.

If the isotherm is nonlinear, the qualitative behavior remains nearly the same as that shown in Figures 5 and 6. The quantitative performance is changed, however, and in many cases the breakthrough curves are “sharper” (steeper) when plotted on the relative-concentration and relative-time coordinates. The effect of equilibrium can be explained in terms of an elementary classification that is based upon the Langmuir isotherm equation. Use of this equation is equivalent to defining a new value of a separation factor, R , for each different level of solute concentration in the feed.

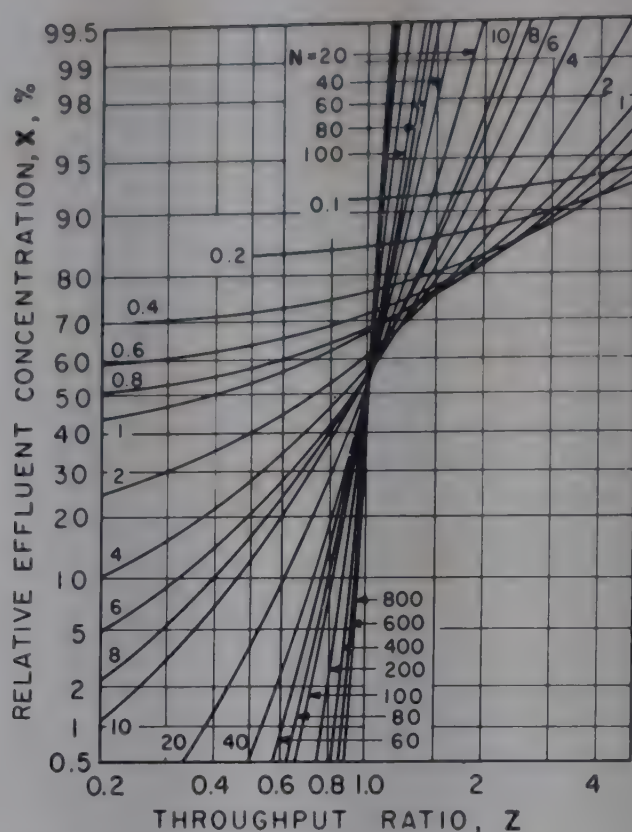


Fig. 6. Breakthrough concentration curves (linear isotherm).
Courtesy *Chemical Engineering Progress*.

The Langmuir isotherm can be represented by

$$\frac{q}{q_{\text{lim}}} = \frac{Kp}{1 + Kp}$$

where q is the solid-phase concentration, weight (or moles) of solute per unit weight of solute-free solid; q_{lim} is the asymptotic upper-limit value of q ; K is the equilibrium constant; and p is the partial pressure of solute, which can be replaced by fluid-phase concentration, c , for a liquid feed. A given solute concentration in the feed to a column, p_0 , corresponds to a saturation value of the solid-phase concentration, q_0^* , conforming to the above equation; it also corresponds to a particular value of the separation factor,

$$R = \frac{1}{1 + Kp_0}$$

With $X = p/p_0$, the isotherm in terms of the dimensionless parameters follows the equation

$$Y = \frac{q}{q_0^*} = \frac{X}{X + R(1 - X)}$$

Figure 7 shows three representative isotherms in the solid curves. Curve ABF corresponds to $R = 0.04$; ACF, to $R = 0.2$; and ADF, to $R = 1$.

The smaller the value of R , the more favorable, or more nearly irreversible, the equilibrium becomes. A decrease in R is accompanied by a sharpening of the dimensionless breakthrough curves. This effect for a constant relative bed length ($N = 40$) is shown in Figure 8.

A value of R greater than 1 corresponds to unfavorable equilibrium. The limiting behavior of such systems has been discussed by DeVault (5) and Walter (27). Al-

though isotherms with R greater than unity are not usually encountered in the saturation step of an adsorption process, this case arises frequently in the desorption (or regeneration) step. Unless the process conditions are altered so as to shift the equilibrium, R for the elution step is equal to the reciprocal of R for the saturation. This

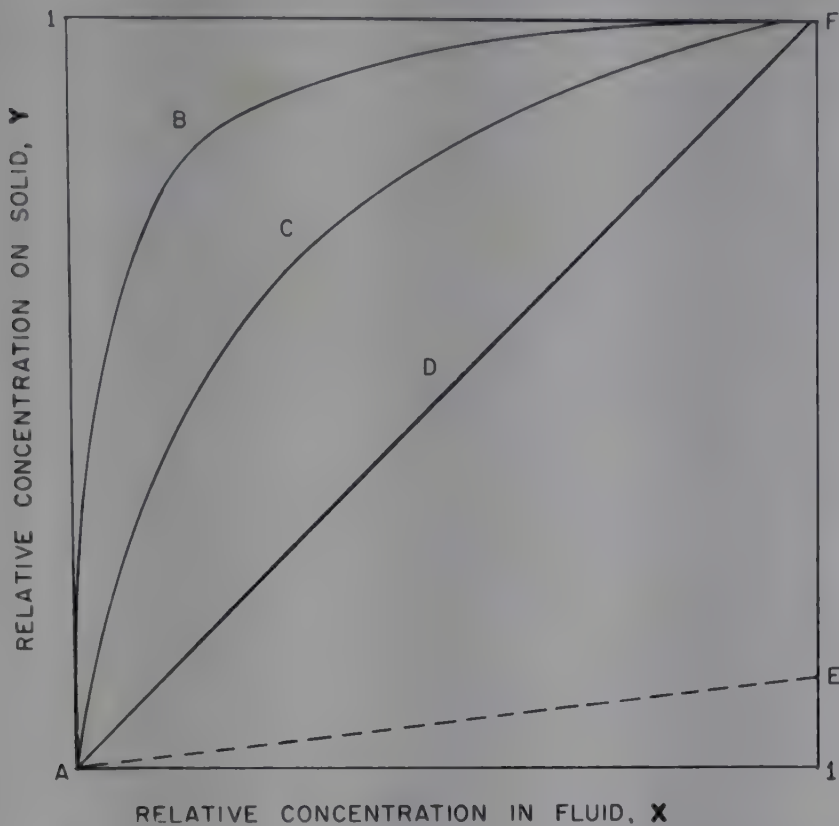


Fig. 7. Relation of separation factor to isotherm shape.

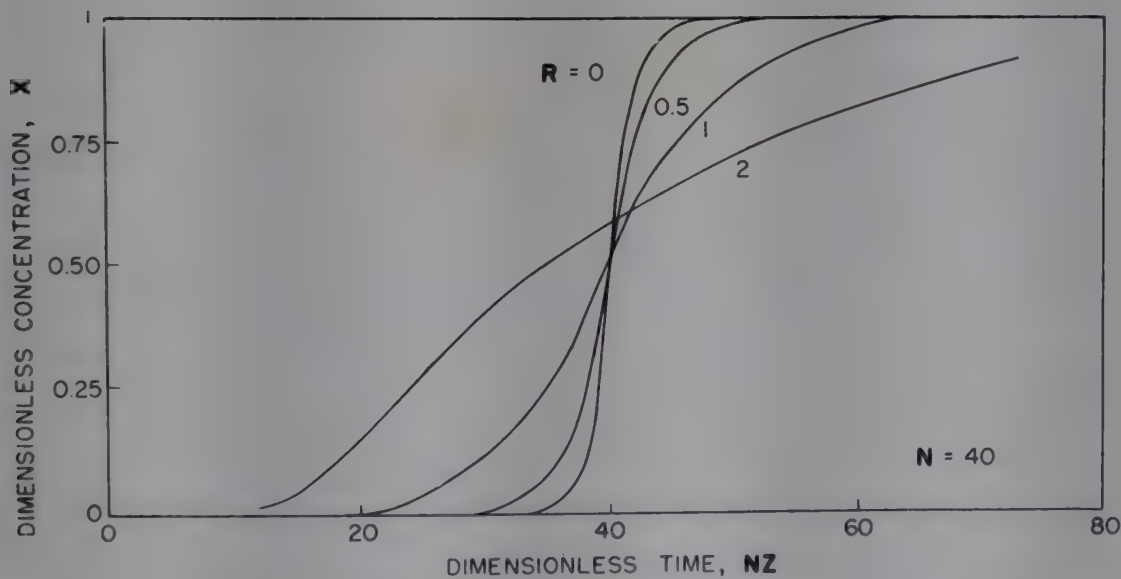


Fig. 8. Effect of separation factor on sharpness of breakthrough curve, at constant N . Courtesy Academic Press, Inc.

leads to the result that a very favorable saturation, with small R , is accompanied by a very unfavorable desorption with large R .

In order to overcome this difficulty, desorption is usually conducted under conditions of markedly changed equilibrium. This is accomplished by raising the temperature, by reducing the pressure in a gaseous system, or by changing the carrier fluid in a

liquid system. Such a change has the effect of reducing R for the elution step to a value well below unity, thereby insuring a sharp and efficient removal of solute from the column prior to its reuse in the next cycle. The theoretical significance of the shifted equilibrium can be understood by referring again to Figure 4. In desorption the X value moves from right to left, and the Y value from top to bottom of the diagram. These changes in direction are equivalent to rotating the diagram through 180° , thus making the isotherms concave upward and raising their R values above unity. The shifted equilibrium corresponds to the desorption path FEA. Once again this is seen to represent a nearly irreversible path, yielding the desired sharpness of breakthrough.

For the numerical calculation of breakthrough curves, a plot similar to Figure 6 is needed for each separate value of R . However, for R values less than about 0.5, the algebraic equations for X , in terms of R , N , and Z or NZ , are simplified greatly and can be used instead of computed curves. The linear equilibrium has been treated by Hougen and Marshall (11), Thomas (22), and Klinkenberg (13). The general non-linear case has been discussed by Thomas (21), Gilliland and Baddour (8), and Hiester and Vermeulen (10,24).

The results at low R are based on a "constant pattern" treatment in which the column behaves similarly to a truly countercurrent system. In this region, the exact shape of the breakthrough curves depends upon the mechanism of the rate-determining step. The fluid-phase resistance case has been solved by Michaels (19); solid-phase diffusion by Glueckauf and Coates (9), and Vermeulen (25); and pore diffusion, approximately, by Acrivos and Vermeulen (2). The reaction-kinetic behavior for $R = 0$ was first treated by Bohart and Adams (3); Treybal (23) has provided a graphical treatment for the case in which a favorable equilibrium isotherm is given numerically rather than in equation form.

In *adsorption chromatography*, the slope of the leading edge of a solute band is determined by the saturation-step value of R , and that of the trailing edge by the elution R . If the ratio of R 's is much different from unity, the result is a highly skewed band which generally gives a poor separation from other bands. Hence, chromatographic separations are usually carried out under such conditions that the isotherm is nearly linear (26).

Breakthrough calculations based on an isotherm are applicable only to systems which are practically isothermal, that is, where the heat of adsorption is small enough to keep the local bed temperature within a range wherein the equilibrium remains nearly constant. Concentration histories, for *adiabatic* nonisothermal adsorption have been described by Derr (4) and Ledoux (16), and can be estimated by Acrivos' stepwise calculation method (1). When such a result is different from the isothermal calculation, it will usually be a closer approximation to the actual performance of the column.

The calculational framework given above can be shown to apply also to *exchange adsorption* in which the solid phase remains continually in a saturated condition but with one solute displacing another. We define new dimensionless concentrations, x and y , based on different reference values than before, and a new separation factor, r , such that x , y , and r conform to exactly the same mathematical relations as do X , Y , and R . By definition, we have

$$x = \frac{p_A}{p_A + p_B} \quad \text{or} \quad \frac{c_A}{c_A + c_B}$$

Solid-phase saturation is indicated by

$$q_A + jq_B = \text{const.} = q_{\max}$$

with j a constant which may equal unity. The Langmuir isotherms for the components combine to give

$$\frac{q_A}{jq_B} = \frac{K_A}{jK_B} \cdot \frac{x}{1-x} \text{ which yields } \frac{q_A}{q_A + jq_B} = \frac{x}{x + \frac{jK_B}{K_A}(1-x)}$$

If the left-hand term (equal to q_A/q_{\max}) is identified as y , and jK_B/K_A as r , an exact correspondence is obtained with the previous equation for Y . Figure 9, from the work of Mair, Westhaver, and Rossini (17) shows an exchange-adsorption system to which these calculation methods can be applied.

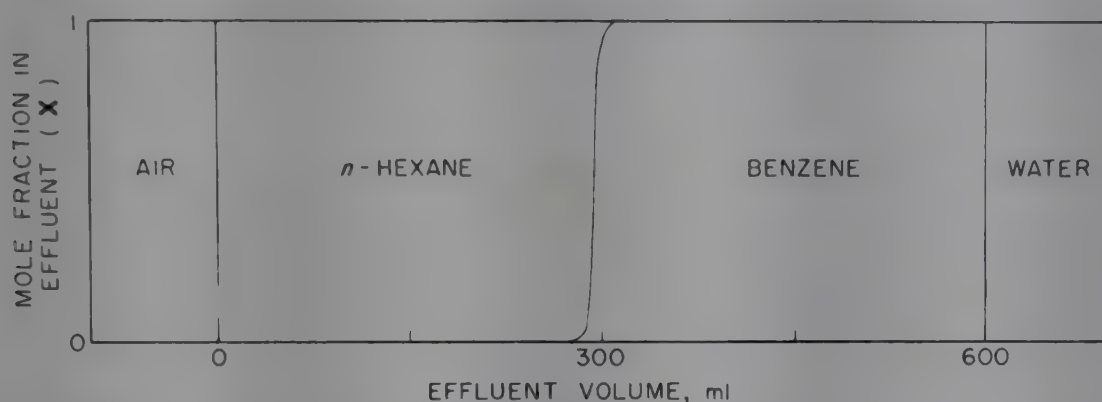


Fig. 9. Exchange-adsorption breakthrough. Hexane-benzene-water on silica gel.

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AEROSOLS

In the strict sense of the word, an aerosol is a colloidal system in which finely divided liquids or solids, usually within the range 10-50 μ , are dispersed in a gas (1). This article, however, is concerned with the "aerosol" industry, in which the term refers to "self-dispensing, pressurized, self-propelling products, dispensed by the use of a liquefied, nonliquefiable, or noncondensable gas" (2). The Chemical Specialties Manufacturers Association, which encompasses practically all companies closely related with the industry in the United States, takes a slightly narrower view of the meaning of the term when it defines an aerosol as a "self-contained sprayable product in which the propellant force is supplied by a liquefied gas" (3).

The modern aerosol industry has developed since World War II. It uses, as propellents, largely certain chlorofluorohydrocarbons, to a small extent several hydrocarbons, and some other substances to a minor extent. There were forerunners of the industry as far back as the beginning of the century. In the first comprehensive review of the history of the industry, Shepherd (4) cited patents dating from as early as 1899 in which methyl and ethyl chloride were used as the propellents, and he comments that the reader "familiar with modern aerosol technology will recognize how close Helbing and Pertsch (the inventors) were to the products destined to appear on the market almost half a century later."

Pharmaceutical products, perfumes and colognes, and even materials dispensed as foams were the subjects of patents issued from 1903 to 1933 for compositions that would now be described as aerosols. In certain instances, it is known that such products were actually marketed.

The first fluorinated hydrocarbons were developed in the search for nontoxic refrigerating gases. These included, among others, dichlorodifluoromethane, and early workers were aware of its value for the purpose of propelling either itself or other substances out of a container. In 1935, the use of this substance as a fire-extinguishing propellant was patented.

In the early years of World War II, Goodhue and Sullivan (5,6), in working on methods of applying insecticides, found that they could incorporate the active ingredient into a solution with the liquid refrigerant gases, and the latter acted to propel

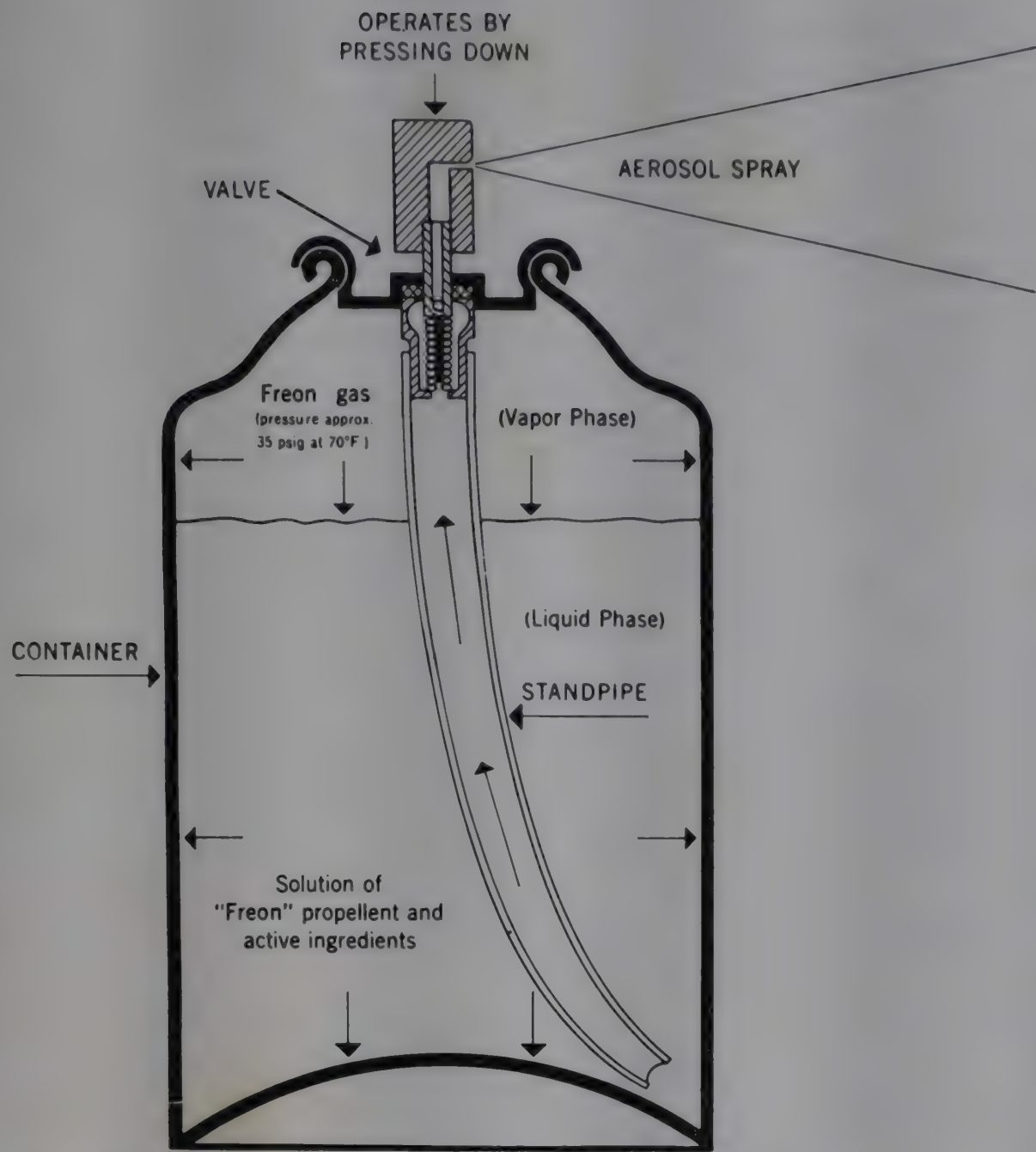


Fig. 1. Cross section of typical space or surface spray aerosol package with Freon as the propellant.

the contents from the container upon release of a valve (Fig. 1). Thus, the insecticide could be dispensed into the air or on a surface. Literally millions of aerosol insecticidal bombs were made during the war on the basis of this work.

Propellents

As defined by the Chemical Specialties Manufacturers Association (3), a propellant (also spelled propellant) is a "liquefied gas with a vapor pressure greater than atmospheric pressure (14.7 psia) at a temperature of 105°F." This definition is not exactly the same as that used in the common parlance of the industry in that it does not include nonliquefiable gases, such as air and nitrogen, and such compressed gases as carbon dioxide and nitrous oxide, all of which are used as the propelling or energy-giving sources in aerosol systems.

Requirements for a Propellent. The requirements for a propellent must be worked out in conjunction with the nature of the container, the pressure and spray pattern desired, and other vital factors. Reed (7) has summarized the following general requirements which must be met by all propellents, under all circumstances:

1. A fluorinated hydrocarbon propellant must have a vapor pressure falling somewhere between 15 and 100 psig, as computed at 70°F. (The Fahrenheit system is invariably used in the aerosol industry in the United States, probably because the propellant literature was first developed for the refrigerating industry where this system still prevails.) Vapor pressures above 100 psig will prove dangerous in containers presently in use in the United States, and probably elsewhere, although stronger containers with a greater margin of safety could be devised, if demand existed.

Table 1. Physical Properties of the Halogenated Propellents. Methane Series (8)

	Propellant				
	11	12	21	22	30
chemical name	trichloro-monofluoromethane	dichlorodifluoromethane	dichloromonofluoromethane	monochlorodifluoromethane	dichloromethane
formula	CCl_3F	CCl_2F_2	CHCl_2F	CHClF_2	CH_2Cl_2
molecular weight	137.4	120.9	102.9	86.5	84.9
boiling point, °F	74.8	-21.6	48.1	-41.4	105.2
freezing point, °F	-168	-252	-211	-256	-142
vapor pressure, psig					
70°F	13.4 ^a	70.2	8.4	122.5	7.1 ^a
130°F	24.3	181.0	50.5	300	9.0
liquid density, g/ml					
70°F	1.485	1.325	1.323	1.209	1.325
130°F	1.403	1.191	1.193	1.064	
vapor density at bp, g/l	5.86	6.26	4.57	4.83	3.30
heat of vaporization at bp, Btu/lb	78.31	71.94	104.2	100.7	141.7
liquid viscosity, cps					
70°F	0.439	0.262	0.351	0.238	0.441 ^b
130°F	0.336	0.227	0.286	0.211	
liquid thermal conductivity at 70°F, Btu/(hr)(ft ²)(°F/ft)	0.063	0.051	0.072	0.063	0.089 ^b
surface tension at 77°F, dynes/cm	19	9	19	9	28 ^b
solubility in water at 70°F, wt %	0.009	0.008	0.13	0.12	0.17 ^c
flammable limits, vol % in air	none	none	none	none	none
toxicity, UL rating system ^d	5	6	(5) ^e	5	4-5

^a In psia.

^b At 68°F.

^c At 77°F.

^d Underwriters' Laboratories classification Group 6 indicates the lowest toxicity, and lower numbers indicate higher toxicity.

^e Much less toxic than 4, slightly more toxic than 5.

2. It is expected that a propellant will be relatively nontoxic, particularly inasmuch as some of the material may be inhaled. All propellents presently in use meet this requirement, and in fact extremely few allergic reactions attributable to the propellents have been reported. The question of toxicity becomes particularly acute for food aerosol and oral hygienic products, and is more important for a room deodorant

or a surface coating that will be sprayed in rather large quantities in a confined area than for a garden spray for a rose bush, for example.

3. It is expected that a propellant will be chemically inert, not only to avoid interference with or reaction with the active ingredients, but to avoid or even inhibit corrosion of the can.

4. A propellant must be both nonflammable and nonexplosive, characteristics which are particularly well met by the fluorinated hydrocarbons. This does not mean that the total system in which the propellant is used is necessarily nonflammable. Obviously, a hair spray or a room deodorant containing ethyl alcohol will be nonflammable only when the proportion of alcohol to fluorinated hydrocarbon is relatively low. When the proportions are reversed the system may lose its nonflammability, or even become highly flammable.

While the above are the main requirements, Reed mentions several others which would seem to be desirable, in certain if not in all instances: freedom from odor and color, good solvent power, freedom from irritation, and a cost structure that is practical for economic use.

Fluorinated Hydrocarbons. Most aerosols now produced commercially, except for foods, shaving cream, and some minor products, are using fluorinated hydrocarbons as the source of energy. Among the fluorinated hydrocarbons, the main propellents currently in use are shown in Tables 1, 2, and 3. The accurate chemical nomenclature is today seldom used outside the patent and occasionally some technical literature.

Table 2. Physical Properties of the Halogenated Propellents. Ethane Series (8)

	Propellant				
	114	114a	142b	152a	160
chemical name	1,2-dichloro-1,1,2,2-tetrafluoroethane	1,1-dichloro-1,2,2-tetrafluoroethane	1-chloro-1,1-difluoroethane	1,1-difluoroethane	chloroethane
formula	CClF ₂ CClF ₂	CCl ₂ FCF ₃	CClF ₂ CH ₃	CHF ₂ CH ₃	CH ₃ CH ₂ Cl
molecular weight	170.9	170.9	100.5	66.1	64.5
boiling point, °F	38.4	37.8	15.1	-11.2	12.2
freezing point, °F	-137	ca -76	-204	-179	-139
vapor pressure, psig					
70°F	12.9	13.4	29.1	61.7	5.0
130°F	58.8	60.6	97.2	176	41.3
liquid density, g/ml					
70°F	1.468	1.478	1.119	0.911	0.920
130°F	1.360	1.371	1.028	0.813	
heat of vaporization at bp, Btu/lb	59.0	58.2	96.0	141	
liquid viscosity, cps					
70°F	0.386	0.463	0.330	0.243	
130°F	0.296	0.347	0.250	0.186	
solubility in water at 70°F, wt %	0.008	0.006	0.054	0.17	
flammability limit, vol % in air	nonflammable	nonflammable	9.0-14.8	5.1-19.1	3.7-12.0
toxicity, UL rating system	6	6 ^a	5 ^a	6 ^a	4

^a Probable.

The materials are denoted by trade names, followed by a number, as Freon-11, Genetron-11, or Isotron-11, and others. In 1961, to avoid confusion, all commercial producers agreed to adopt the same numbering system, and publications started to refer to the products as Propellent-11 (or Propellent-12, Propellent-114, etc).

The numbering system that has grown up is complicated, cumbersome, and expresses to most chemists and chemical engineers working with these products little more than a shorthand method of identifying the substance, but without identification of its structure. In this respect, it cannot be compared with accurate chemical nomenclature, although Reed points out that the numerals do indicate the number of atoms of fluorine, hydrogen, chlorine, their isomeric arrangement, and other information. (See Fluorine compounds, organic.)

Table 3. Physical Properties of the Halogenated Propellents. Butane Series (8)

	Propellent C318 ^a	Propellent 318
chemical name	octafluoro- cyclobutane	decafluoro- butane
formula	$\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2$	$\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_3$
molecular weight	200.0	238.0
boiling point, °F	21.1	28.4
freezing point, °F	-42.5	< -112
vapor pressure, psig		
70°F	25.4	19.3
130°F	92	76
liquid density at 70°F, g/ml	1.513	1.512
heat of vaporization at 70°F, Btu/lb	46	41.4 ^b
liquid viscosity at 70°F, cps	0.455	
flammability limit, vol % in air	nonflammable	nonflammable
solubility in water at 70°F, wt %	0.014	
toxicity, UL rating system	6 ^c	6 ^c

^a The letter C indicates a cyclic compound.

^b At boiling point.

^c Preliminary value.

Other Propellents. Traditionally the earliest aerosols were based on ethyl chloride and nitrous oxide. After the development of the fluorinated hydrocarbon propellents, and specifically following their first use in insecticides, interest in all other propellents diminished, except for food products where compressed soluble gases (carbon dioxide and nitrous oxide) are used. Later, the nonfluorinated products again came into vogue: nitrogen primarily for dental cream, and hydrocarbons devoid of any fluorine in the molecule, following an extended patent suit in which the use of the fluorinated propellents in certain foam products was restricted to the patent holder.

The physical constants and properties of the main propellents other than the fluorinated hydrocarbons are given in Table 4.

Propellent Mixtures. In addition to the use of one propellent in an aerosol system, propellents in combinations with each other are often used to obtain the desired density, vapor pressure, and other effects. Thus, a combination of Propellent-11 and Propellent-12, in a 50/50 proportion, will have a liquid density of about 1.40 and a vapor pressure of about 20 at 70°F. The liquid density is about the midpoint

Table 4. Physical Properties of the Hydrocarbon and Nonliquefied Gas Propellents (8)

	Propane	Isobutane	n-Butane	Carbon dioxide	Nitrous oxide	Nitrogen	Air
chemical formula	CH ₃ CH ₂ CH ₃	(CH ₃) ₂ CHCH ₃	CH ₃ (CH ₂) ₂ CH ₃	CO ₂	N ₂ O	N ₂	N ₂ + O ₂
molecular weight	44.1	58.1	58.1	44.0	44.0	28.0	29
boiling point, °F	-43.9	13.6	30.9	-109 ^a	-127	-320	
freezing point, °F	-275	-229	-211				
vapor pressure, psig							
70°F	110	31	16	837	720	477 ^b	
130°F	260	96	66				
liquid density at 68°F,							
g/ml	0.5005	0.5788	0.5571				
heat of vaporization,							
Btu/lb	183.1	165.6	157.5				
flammable limit, vol %							
in air	2.3-7.3	1.8-8.4	1.6-6.5	nonflam	nonflam	nonflam	nonflam
toxicity, UL rating sys-							
tem	5	5	5	5		6	6
solubility in water at							
77°F ^c				0.7	0.5	0.014	0.017

^a Sublimes.
^b At critical point, -233°F.
^c Volume of gas at atmospheric pressure soluble in one volume of water.

between the same property for Propellent-11 and Propellent-12 (1.485 and 1.325, respectively). But Propellent-11 has a vapor pressure of 13.4 psia and Propellent-12, a vapor pressure of 70.2, so that the vapor pressure of the mixture could not be predicted by any simple interpolation.

Mixtures of nonfluorinated hydrocarbons have also been employed; also, for food products, mixtures of carbon dioxide and nitrous oxide have been used in various proportions.

Containers

From the beginning of the American aerosol industry the principal containers in use have been made of tinplate. In addition to tinplate containers, there are glass bottles on the American market, some plastic containers (although they have not been particularly successful), aluminum containers (more widely used on the European continent than in the United States), and occasionally containers of stainless steel. Glass and plastic containers accounted for less than 10% of the containers filled by leading U.S. aerosol fillers in 1960; they are used largely for colognes and perfumes.

The *tinplate containers* now in commercial use come in various shapes and sizes; the most popular sizes are 4, 6, 10, 12, and 16 oz (fluid ounces of total capacity). These containers usually are not filled to maximum capacity inasmuch as there is a greater safety factor with the smaller fill; thus, an 8-oz container may have a fill of either 6 or 7 oz. Less than 6 oz, however, would be considered a slack fill for an 8-oz container, for although the net contents are stated prominently on the label, many authorities hold that the larger appearance with the smaller amount would give a false impression.

The inner side of the containers may be either bare or coated. Coated containers are usually made specifically for a given product. Thus, different internal coatings are necessary for shaving cream, for shampoos, for quaternary ammonium disinfectants, and other products.

The *glass bottles* may be uncoated, coated with a plastic coating, or encased in a metal container. Glass offers the advantages of ease of design and decoration to make

attractive products, particularly for cosmetic use, and of excellent freedom from corrosion. Widely variable shapes can easily be made for individual customers. Glass, if coated, is usually considerably more expensive than metals; if uncoated, it is slightly higher priced than most metals, and although many important measures have been taken to insure the safety of the container and to protect the user, no container can be as safe as one of metal.

Aluminum, in the opinion of Thomas (9), is least resistant to corrosion of all commercial materials for aerosol use. It has light weight and, like other metals, will not break.

Stainless steel has been limited to small containers requiring a spray pattern that could not be achieved save with Propellent-12 (dichlorodifluoromethane), and usually has been used for pharmaceuticals.

Valves

Probably the most important single part of the aerosol system, aside from the propellant, is the valve. The valve is a small mechanism which can be opened at will, and usually (although not always) will remain open so long as pressure is applied, as from the finger. While the valve is open, the vapor pressure of the propellant in the system forces liquid (mixed propellant and active ingredients) through the temporarily open mechanism. When the pressure from the finger is discontinued, the valve springs back into its original or closed position, causing an almost airtight seal.

There are numerous variations of the above mechanism, one of which is the metered valve, which permits the escape of a limited and measured amount of a material and reseals, automatically, regardless of the length of time that the finger is held on the actuator or button part of the valve. The amount of material released with each act of opening is thus held more or less constant; it is said to be measured, metered, or, in what may be considered a misuse of the word, "calibrated."

Variations in valve design permit changes in the rate of dispensation of material, the pattern of spray, the direction of spray, the size of the aerosol particles, and other characteristics of the finished product.

Special valves have been designed for various products, containers, and desired features, although certain valves are usable on a wide variety of products. There are valves for dispensing powdered materials, which present the packager with a special problem: how to prevent leakage or seepage of the propellant that might be caused by small granules of the powder setting on the valve mechanism and thus preventing complete closure.

A special mechanism, known as the one-shot valve, has attained some degree of popularity with the aerosol fire extinguisher. Another mechanism, known as reuse valve, has attained greater popularity in Europe than in the United States. Commercial products have been marketed with transfer valves that permit the refilling of a smaller container (usually purse-size) from a larger one with relatively little effort on the part of the customer. Special variations in the construction of the valve are necessary for nitrogen-propelled products, paints, foam products, and other uses.

Although most valves seal very tightly so that, if not tampered with, the contents remain intact over an almost indefinite period of time, a special hermetically sealed valve has been constructed, but its use is expected to be limited to extraordinarily sensitive pharmaceutical products.

Structure of the Aerosol Industry

In addition to manufacturers of propellents, containers, valves, and numerous components used in the formulation of the contents, the aerosol industry includes a group of companies known as loaders or fillers, and another group known as merchandisers. In some instances, merchandisers are also loaders.

Most of the larger fillers in the industry, at least in the United States, are contract manufacturers or private-label manufacturers not engaged in the manufacture and sale of products for themselves or for a subsidiary. Most of these firms engage in private-label manufacture only for their customers. Inasmuch as aerosol loading is a highly specialized technique, these companies, for the most part, do not engage in conventional—ie, nonaerosol—manufacture and filling.

Some aerosol fillers do, however, engage in nonaerosol manufacture and filling, likewise on a private-label basis. Some companies, although primarily contract manufacturers, have not only a sales department and a product line of their own, but market products under a trade name wholly owned and controlled by themselves. On the other hand, there are cosmetics, paint, and other companies that engage in the manufacture of aerosols on their own premises and in their own equipment.

Although no breakdown is available, it is probably true that a large majority of the total number of cans (and bottles) produced in the United States and Canada are filled by contract manufacturers who are not engaged in the merchandising and distribution of these products.

Economic Aspects

The 1960 survey of aerosol production in the U.S. and Canada made by the Chemical Specialties Manufacturers Association (10) covered all nonfood pressurized products. Of the 216 companies having aerosol filling lines and from whom figures

Table 5. Nonfood Aerosol Production in U.S. and Canada, 1960

Product	Containers, millions
insect sprays	82.5
coatings	68.2
room deodorants	81.8
glass cleaners	19.7
shoe or leather dressings	17.4
starches	24.8
waxes and polishes (household and automotive)	40.2
other household products	24.0
hair sprays and dressings	116.9
medicinals and pharmaceuticals	13.8
perfumes and colognes	42.0
shaving lather	68.2
other personal products	12.9
veterinarian and pet products	4.7
deicers	14.2
miscellaneous products	20.7
all other categories not reported individually	18.2
total	670.2

were requested, 128 replied, but these 128 included all the major producers, and over 90% of the production. The CSMA was able to make estimates for the production of the remaining producers, and gave the total figures shown in Table 5.

Although no survey was made of aerosol food production, the container companies reported that they had sold almost 60 million containers for food products in 1960, and it can be assumed that this figure is close to the number of units filled.

It is interesting to note that in 1946 the youthful aerosol industry produced less than 4 million units; in 1950, production was still only 30 million. It is clear that the industry has been growing extremely rapidly, and the market has not yet reached the saturation point.

Applications

The most important commercial products now being packaged in the United States in aerosol form, as examination of Table 5 will reveal, are hair sprays, room deodorants and other air refreshers, shaving cream, perfumes and colognes (see Cosmetics), insecticides, paints and other surface coatings, some miscellaneous household products, and whipped cream.

Several score of other products have been marketed, and continue to be marketed, some of them attaining commercial success. An exhaustive list of aerosol products should include the general categories of cosmetics and toiletries (other than those mentioned above), various pharmaceutical preparations, and large numbers of household and industrial specialties. A few highlights of some of these products are given below.

Hair Sprays. Hair sprays or hair lacquers constitute one of the most successful types of aerosol products. In addition to the fluorinated hydrocarbon propellant and ethyl alcohol, these products have been based either on shellac or on polyvinylpyrrolidone (PVP), or both, the former giving a spray more resistant to moisture than the latter. A patent restricting the use of PVP was granted (11,12), resulting in the search for new resins including but not limited to copolymers of PVP.

Other Hair Products. Efforts were made to launch aerosol shampoos for many years. The first products to be marketed produced corrosion of the can, and had to be withdrawn. Several years later, noncorroding shampoos were formulated and merchandised. A novelty of these products was "lazy foam," for the product came forth from the can as a stream, but foamed instantly upon reaching the hand or hair. These products have maintained only a small part of the total shampoo market.

Other hair cosmetics in aerosol form have included foam and spray hair dressings propelled either by fluorinated hydrocarbons, saturated hydrocarbons, or nitrogen, also brilliantines, the latter consisting of a lanolin-mineral oil combination that is perfumed and packaged with propellant under pressure.

Room Deodorants and Air Refreshers. The space deodorant field, in which the aerosol products dominate, consists of household air refreshers, air sanitizers, chemical deodorizers, and specially formulated products for spraying in automobiles, children's nurseries, and elsewhere. All products in this category contain perfume as a major component. Some products also have bactericidal or bacteriostatic ingredients, which produce a more sanitary atmosphere and prevent the development of bad odors that come about through bacterial decomposition; or they may contain oxidizing agents or other substances that react chemically with odoriferous substances to create either nonodorous or less unpleasantly odorous materials.

Shaving Cream. Aerosol shaving cream is the most popular single form of shaving product in the United States. Traditionally, these products were unstable emulsions, based on stearic acid, triethanolamine, and other components, and propelled by mixtures of Propellent-12 and Propellent-114. Following a prolonged patent suit (13), attention turned to the manufacture of shaving cream with saturated hydrocarbon propellents. According to Prussin (14), "The liquefied petroleum (saturated hydrocarbon) propellents used for shaving cream usually consist of butane or isobutane in conjunction with propane to achieve the desired pressure. . . The manufacturing hazards in no way affect the finished product, which is safe for use, completely non-flammable, and less expensive than its halogenated hydrocarbon equivalent."

Toothpaste. Toothpaste formed a landmark in the history of aerosol technology because it was based on the use of nitrogen as a propellant, and on the solving of certain problems involving valve and other components, concomitant with the utilization of nitrogen. Although the product as marketed was cosmetically elegant, it has not achieved lasting commercial success, has held only a small part of the market, and may have to conduct a great struggle even to survive as a minor factor.

Fragrance Products. An important part of the total fragrance business in the United States is now centered in the aerosol package. Perfumes are usually manufactured in metered-spray form. Colognes, in coated or uncoated glass bottles, may or may not have metered-spray valves. Many of these packages have outward elegance equal to that of the nonaerosol perfume or cologne. Closely associated with perfume and cologne is the sachet mist, a special air deodorizer often lavender in character, designed for imparting a desired fragrance to linens, laundry, and closets.

Insecticides. Total aerosol insecticides for home use are produced in greater quantities in the United States than the corresponding nonaerosol products. Originally based on Propellent-12, they were later formulated with lower pressure and, in most instances, a combination of Propellent-11 and Propellent-12. Products include contact insecticides and residual insecticides, as well as garden toxicants and insect repellents for special purposes.

Pharmaceutical Aerosols. Pharmaceutical aerosols are still in their infancy, but several products have been marketed with considerable success. These include a protective-film-type skin bandage, and sprays for athlete's foot, poison ivy, antibiotic sterilization, burn relief, topical anesthetics, and nasal sprays.

Surface Coatings. Although aerosol paint is more expensive than the gallon can with the conventional brush or roller, it is exceptionally easy to apply, and gives excellent results, even to the traditionally unhandy husband who boasts that he cannot drive a nail into a piece of wood. For touch-up purposes, as well as general small-surface painting, it is being widely used. Clear acrylic lacquers are also used as a protection for art work and other surfaces.

Food Aerosols. Most successful of the food aerosols is whipped cream. Food toppings and flavors have also been marketed, and some dozen or more products are under careful study and test. While new fluorinated hydrocarbons have been developed for use in food products, the foods thus far marketed have been propelled by compressed soluble gases—carbon dioxide, nitrous oxide, and nitrogen.

Household and Industrial Specialties. Aside from the broader categories mentioned above, there are several score of products that are today being marketed for household or industrial use. These include the recently launched deicers and starch, as well as fire extinguishers, window cleaners, furniture polish and automotive polish,

artificial snow, oven cleaners, spot removers, charcoal igniters, shoe polish, and many others.

In addition, there are numerous other aerosol-packaged cosmetics and toiletries. Aerosols, both foam and spray, have been marketed for body deodorants, sunscreening agents, hand and body lotions and creams, and for most other cosmetics, except makeup.

Aerosol technology is still in its early years. Less than twenty years after the work of Goodhue and Sullivan, which marked the beginning of the modern aerosol industry, two major volumes on the subject have appeared (4,15). Improvements in valves and containers are under study; new coatings are constantly being tested; hundreds of products not yet marketed in pressurized form are the subject of research studies; and new propellents are being synthesized. It is not difficult to envisage continued expansion of this growing field in the years ahead.

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MAURICE S. SAGE
Sage Laboratories, Inc.

AGAR. See Seaweed colloids.

AGAVE. See Sisal under Fibers, vegetable.

AGRICULTURAL CHEMICALS. See Fertilizers; Fungicides; Insecticides; Soil chemistry; Weed killers.

AIR CONDITIONING

Air conditioning as defined by the American Society of Heating, Refrigeration, and Air-Conditioning Engineers is "the process of treating air so as to control simultaneously its temperature, humidity, cleanliness, and distribution to meet the requirements of the air-conditioned space."

Air conditioning is probably most often thought of in terms of human comfort, although the art had its beginnings in the field of industrial processing, and it is in industry where its most significant developments have taken place. Although considered as one of the newer arts and sciences, air conditioning has been a practical industrial tool since about 1902. At about this time, Dr. Willis H. Carrier developed and designed what came to be known as the world's first true "air conditioning" system for the Sackett-Wilhelms printing plant. This system provided a means of controlling the moisture in the air which was a serious problem in the printing industry. Also, at about this time, Dr. Carrier first applied this system to a cotton mill for the control of temperature and humidity, controls which had been wholly lacking in textile mills. From the mill, Dr. Carrier rapidly extended the application of his processes to other industries, and into cooling and dehumidification, as the air-conditioning process readily lent itself to these adaptations.

Since 1911, air conditioning has been a recognized branch of engineering. At that time, Dr. Carrier presented before the American Society of Mechanical Engineers two papers on the subject. One, entitled "Rational Psychrometric Formulae—Their Relation to the Problems of Meteorology and of Air Conditioning," disclosed the results of some nine years of research and mathematical deductions involving psychrometrics. The second paper, "Air Conditioning Apparatus—Principles Governing Its Application and Operation," undertook to describe the operation and design of practical air-conditioning systems. The psychrometric chart presented in "Rational Psychrometric Formulae," since its publication, has served as a basis of all air-conditioning problems. The latest Carrier psychrometric chart, Figure 1, refines some of the data in the original, making it more suitable for accurate scientific work, though the changes are not appreciable in ordinary engineering calculations.

A significant advance in the air conditioning industry occurred in 1921 with Dr. Carrier's invention of the centrifugal refrigeration machine. This development opened vast new fields in comfort and industrial air-conditioning and process refrigeration. Another important advance, at that time, was the application of industrial practices in air distribution and equipment to the air conditioning of large motion-picture theaters. As a result, air conditioning for human welfare and comfort made rapid strides during the next decade; this led to the development of low-cost unitary equipment.

Increasing consideration is being given in industry to the comfort of workers, since studies show that the proper control of temperature, humidity, and air purification in working areas results in higher production, reduced absenteeism, and improved personnel relations.

Principles of Air Conditioning

The art and science of air conditioning are based on the laws of thermodynamics. The air-conditioning industry has developed a specific branch of thermodynamics known as psychrometry, which discusses the physical laws of air-and-water mixtures. Psychrometric charts are widely used for the solution of air-conditioning problems.

Such charts are published in various forms; one of the most widely used is reproduced in Figure 1. The dry-bulb temperature is plotted as abscissa, the ordinate can be read as grains of moisture per pound of dry air (7000 grains = 1 lb). The horizontal lines also indicate lines of constant dewpoint. Sloping lines of constant wet-bulb temperature are ruled in; they represent, for all practical purposes, lines of constant enthalpy and give the path followed on the cooling of air by adiabatic evaporation. Constant relative humidity is represented by a series of curves, the 100%-rh line corresponding to the saturation line. An example of an evaporative cooling cycle is also shown. Similar psychrometric charts are available for temperatures below 32°F, and above 110°F, and for pressures other than 29.92 in.

Below are given some of the more important terms and their definitions as used in the air-conditioning industry:

ABSOLUTE HUMIDITY. The weight of water vapor per unit volume (grains or pounds per cubic foot, or grams per cubic centimeter).

ALIGNMENT CIRCLE. Located at 80°F dry-bulb and 50% rh, this point, in conjunction with the sensible-heat factor, is used to plot the various air-conditioning process lines.

DEHUMIDIFICATION. Commonly used by the industry to denote removal of water vapor from air by condensation, whereby sensible and latent heat are removed simultaneously.

DEHYDRATION. Commonly used to indicate removal of water vapor from air by contact with a solid or liquid that has affinity for water vapor.

DEWPOINT TEMPERATURE. The temperature at which the condensation of water vapor in a space begins for a given state of humidity and pressure as the temperature of the vapor is reduced. This temperature corresponds to saturation (100% relative humidity) for a given absolute humidity at constant pressure.

DRY-BULB TEMPERATURE. The temperature of the gas or mixture of gases as indicated by an unwetted thermometer, shielded from radiation.

ENTHALPY. The quantity of heat in the air, in Btu per pounds of dry air, above an arbitrary datum (0°F for dry air, and 32°F water for the moisture content).

ENTHALPY DEVIATION. Enthalpy, as defined above, is the enthalpy of saturation. When the air is not saturated, correction should be made for the resulting deviation in enthalpy. (This is not necessary for ordinary air-conditioning estimates; for extreme accuracy, enthalpy deviation, also in Btu per pounds of dry air, is given.)

LATENT HEAT. A term used to express the energy involved in a change of state.

RELATIVE HUMIDITY. The ratio of the mole fraction of water vapor in a mixture to the mole fraction of water vapor in saturated air at the same dry-bulb temperature and barometric pressure; also defined in various texts as the ratio of the actual partial pressure of the water vapor in the space to the saturation pressure of pure water at the same temperature.

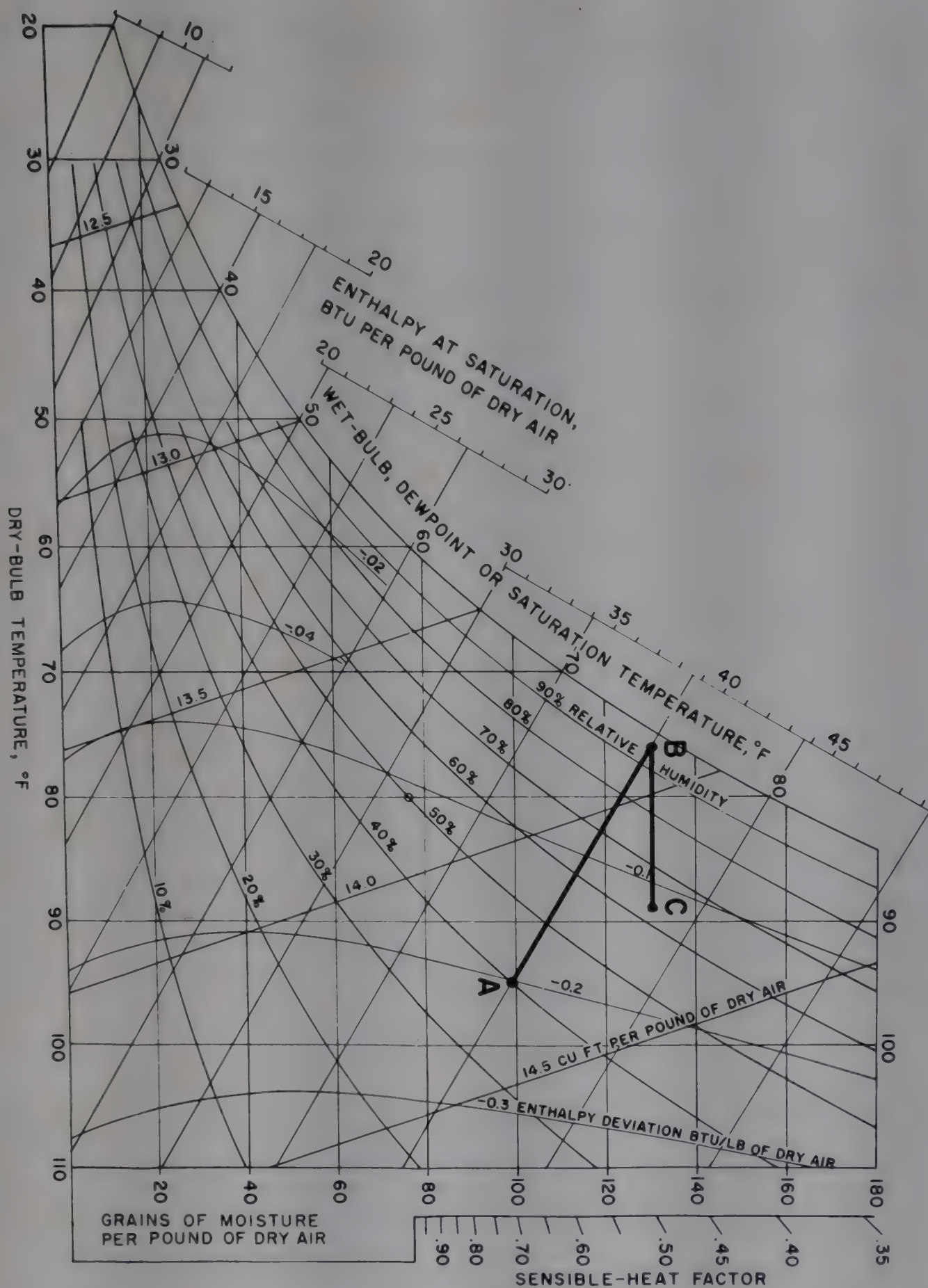


Fig. 1. Psychrometric chart. Example: Air entering at point A, 95°F dry-bulb and 75°F wet-bulb temperature, leaves the spray chamber at point B, 76°F dry-bulb and 75°F wet-bulb (based on 95% washer efficiency). The air then absorbs the sensible heat in the room and produces a room condition, shown at point C, of 89°F dry-bulb and 65% relative humidity (absolute humidity of the room remains constant, if there are no sources of latent heat in the room).

SENSIBLE HEAT. A term used in heating and cooling to indicate any portion of heat that changes only the temperature of the substances involved.

SENSIBLE-HEAT FACTOR. The ratio of sensible to total heat.

VAPOR PRESSURE. The equilibrium pressure exerted by a vapor in contact with its liquid.

WET-BULB TEMPERATURE (without qualification). The temperature indicated by a wet-bulb psychrometer constructed and used according to specifications (*ASME Power Test Codes*, Series 1932, Instruments and Apparatus, Part 18).

Basis for Design

The design of air-conditioning systems is a highly specialized branch of engineering; some of the available texts on the subject are listed in the bibliography. The following discussion gives the general principles of design from the point of view of the prospective purchaser and user rather than the designer.

The selection of temperature and humidity to be maintained depends on three factors: (1) the effect of such conditions on worker comfort and resultant production; (2) optimum temperature and humidity for the product; (3) initial and operating cost of the installation to provide these optimum conditions.

INSIDE COMFORT CONDITIONS

ASHRAE has designed an Effective Temperature Chart, Figure 2. This chart is a tool that can be used to determine space conditions for human comfort. Since comfortable conditions shift on a seasonal basis as the outdoor conditions vary, the chart provides a means of selecting optimum design conditions for summer or winter. It is the result of test work conducted in the ASHRAE Research Laboratory and is the basis for many application designs. Normal practice is to maintain 74–80°F db and 45–55% rh for general comfort in such surroundings as offices, hotels, apartments. For comfort at factories, where process air conditioning is not the prime consideration, conditions are maintained at higher temperatures and humidities, approximately at 77–85°F db and 45–60% rh.

INSIDE INDUSTRIAL CONDITIONS

Table 1 lists typical inside dry-bulb and relative humidities used for preparing, processing, and manufacturing various products, and for storing both raw and finished goods. As technological advances are made recommendations may change. In some instances the conditions have been compromised for the sake of worker comfort and do not represent the optimum for the product. In others, the conditions listed have no effect on the product or process other than to increase worker efficiency.

Specific inside design conditions are required in industrial applications for one or more of the following reasons:

1. A constant temperature is required for close-tolerance measuring, gaging, machining, or grinding operations, to prevent expansion and contraction of machine parts, machined products, and measuring devices. In this instance a constant temperature is normally more important than the temperature level. A constant relative humidity is secondary in importance but should not go above 45% to minimize formation of a surface moisture film.

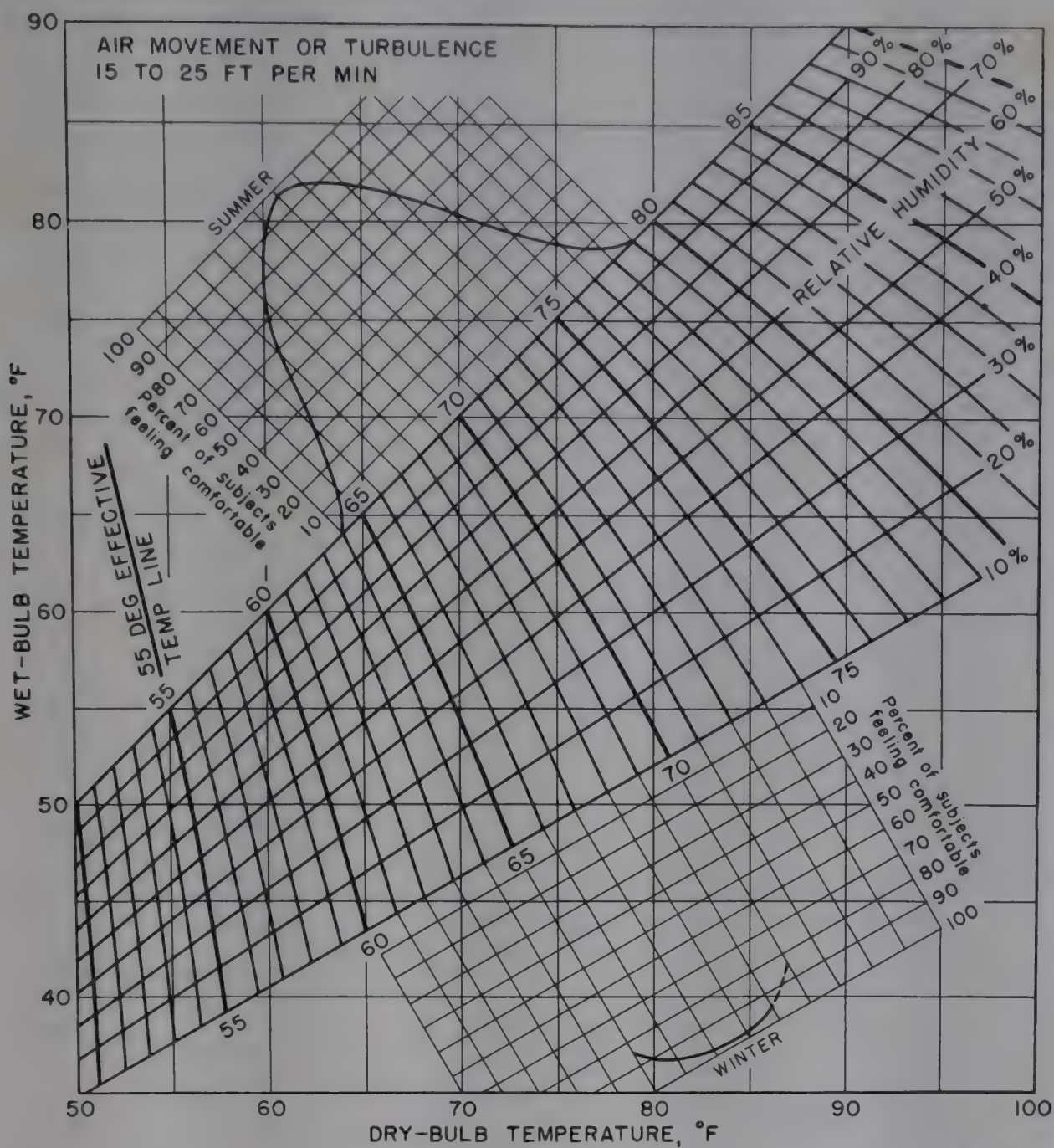


Fig. 2. ASHRAE Comfort Chart.^a Courtesy *Heating, Ventilating Air Conditioning Guide*, 1960.

^a Both summer and winter comfort lines apply to inhabitants of the United States only. Application of the winter comfort line is further limited to rooms heated by central systems of the convection type. The line does not apply to rooms heated by radiant methods. Application of the summer comfort line is limited to homes, offices, and the like, where the occupants become fully adapted to the artificial air conditions. The line does not apply to theaters, department stores, and similar places where the exposure is less than three hours. The summer comfort line shown pertains to Pittsburgh and to other cities in the northern portion of the United States and Southern Canada, and at elevations not in excess of 1000 ft above sea level. An increase of 1°F effective temperature should be made per an approximately five-degree reduction in north latitude.

Nonhygroscopic materials such as metals, glass, and plastics have the property of capturing water molecules within microscopic surface crevices, forming an invisible, noncontinuous surface film. The density of this film increases when relative humidity increases, and must be held below the critical point at which metals may etch or at which the electrical resistance of insulating materials is significantly decreased.

2. Where highly polished surfaces are manufactured or stored for short intervals between different phases of processing, relative humidity and temperature are both

Table 1. Typical Inside-Design Conditions; Industrial^a

Industry	Process	Dry-bulb, °F	Rh, %	Industry	Process	Dry bulb, °F	Rh, %
abrasive bakery	manufacture	75-80	45-50	electrical products	electronic and x-ray:		
	dough mixer	75-80	40-50		coils and transmis-		
	fermenting	75-82	70-75		sion winding	72	15
	proof box	92-96	80-85		tube assembly	68	40
	bread cooler	70-80	80-85		electrical installa-		
	cold room	40-45			tions:		
	make-up room	78-82	65-70		manufacturing		
	cake mixing	95-105			and laboratory	70	50-55
	crackers and biscuits	60-65	50		thermostat		
	wrapping	60-65	60-65		assembly and		
	storage:				calibration	76	50-55
	dried ingredients	70	55-65		humidistat assembly		
	fresh ingredients	30-45	80-85		and calibra-		
	flour	70-75	50-65		tion	76	50-55
	shortening	45-70	55-60		close-tolerance as-		
	sugar	80	35		sembly	72	40-45
	water	32-35			meter assembly test	74-76	60-63
	wax paper	70-80	40-50		switchgear:		
brewery	storage:				fuse and cut-out		
	hops	30-32	55-60		assembly	73	50
	grain	80	60		capacitor winding	73	50
	liquid yeast	32-34	75		paper storage	73	50
	lager	32-35	75		conductor wrapping	75	65-70
	ale	40-45	75		lightning arrestor	68	20-40
	fermenting cellar:				circuit breaker:		
	lager	40-45	75		assembly and test	76	30-60
	ale	55	75		rectifiers:		
	racking cellar	32-35	75		process selenium		
	candy centers	80-85	40-50		and copper		
	hand-dipping room	60-65	50-55		oxide plates	74	30-40
candy (choco- late)	enrobing room	75-80	55-60	furs	drying	110	
	enrobing:			glass	shock treatment	18-20	
	loading end	80	50		storage	40-50	55-65
	enrober	90	13		cutting		comfort
	stringing	70	40-50	leather	vinyl-laminating		
	tunnel	40-45	dp-40		room	55	15
	packing	65	55		drying:		
	pan specialty room	70-75	45		vegetable-tanned	70	75
	general storage	65-70	40-50		chrome-tanned	120	75
	manufacturing	75-80	30-40		storage	50-60	40-60
candy (hard)	mixing and cooling	75-80	40-45	lenses (optical)	fusing		comfort
	tunnel	55	dp-55		grinding	80	80
	packing	65-75	40-45		manufacturing	72-74	50
	storage	65-75	45-50	matches	drying	70-75	40
	drying: jellies, gums	120-150	15		storage	60-62	50
	cold room:				munitions		
	marshmallow	75-80	45-50		metal percussion ele-		
	manufacturing	77	33		ments:		
	rolling	68	63		drying parts	190	
chewing gum	stripping	72	53		drying paints	110	
	breaking	74	47		black-powder drying	125	
	wrapping	74	58		condition and load		
ceramics	refractory	110-150	50-90		powder-type fuse	70	40
	molding room	80	60-70		load tracer pellets	80	40
	clay storage	60-80	35-65		powder storage:		
	decal and decorating	75-80	45-50	pharmaceutical	before manufac-		
	packaging	75-80	45-50		turing	70-80	30-35
	manufacturing	65-70			after manufactur-		
cereal cosmetics distilling	storage:				ing	75-80	15-35
	grain	60	35-40		milling room	80	35
	liquid yeast	32-34			tablet compressing	70-80	40
	manufacturing	60-75	45-60		tablet coating	80	35
	ageing	65-72	50-60		effervescent:		
					tablet and powder	90	15

Table 1 (continued)

Industry	Process	Dry-bulb, °F	Rh, %	Industry	Process	Dry-bulb, °F	Rh, %
pharmaceutical (cont)	hypodermic tablet	75-80	30	textiles (cont)	cotton (cont):		
	colloids	70	30-50		conventional	80-85	60-70
	dough syrup	80	40		long-draft	80-85	
	glandular products	78-80	5-10		frame spinning	80-85	55-60
	ampule manufacturing	80	35		spooling, warping	78-80	60-65
	gelatin capsule	78	40-50		weaving	78-80	70-85
	capsule storage	75	35-40		cloth room	75	65-70
	microanalysis	comfort			combing	75	55-65
	biological manufacturing	80	35		linen:		
	liver extract	70-80	20-30		carding, spinning	75-80	60
photo material	serums; animal room	comfort		weaving	80	80	
	drying	20-125	40-80	woolens:			
	cutting and packing	65-75	40-70	pickers	80-85	60	
	storage:			carding	80-85	65-70	
	film base, film			spinning	80-85	50-60	
	paper, coated			dressing	75-80	60	
	paper	70-75	40-65	weaving:			
	safety film	60-80	45-50	light goods	80-85	55-70	
	nitrate film	40-50	40-50	heavy	80-85	60-65	
	plastic	manufacturing:			drawing	75	50-60
thermosetting				worsteds:			
compounds		80	25-30	carding, combing, and gilling	80-85	60-70	
cellophane		75-80	45-65	storage	70-85	75-80	
plywood	hot press: resin	90	60	drawing	80-85	50-70	
	cold press	90	15-25	cap spinning	80-85	50-55	
precision machining	spectrographic analysis	comfort		spooling, winding	75-80	55-60	
	gear matching and assembly	75-80	35-40	weaving	80	50-60	
	storage:			finishing	75-80	60	
	gasket	100	50	silk:			
	cement and glue	65	40	preparation and dressing	80	60-65	
	machinings:			weaving, spinning	80	65-70	
	gaging, assembly	comfort		throwing	80	60	
	adjusting precision	comfort		rayon:			
	parts	comfort		spinning	80-90	50-60	
	honing	75-80	35-45	throwing	80	55-60	
printing	multicolor lithographing:			weaving:			
	pressroom	75-80	46-48	regenerated	80	50-60	
	stockroom	73-80	49-51	acetate	80	55-60	
	sheet and web printing	comfort		spun rayon	80	80	
	storage, folding, etc.	comfort		picking	75-80	50-60	
	valve manufacturing	75	40	carding, roving, drawing	80-90	50-60	
	compressor assembly	70-76	30-45	knitting:			
rubber-dipped goods	refrigerator assembly	comfort		viscose or cuprammonium	80-85	65	
	testing	65-82	47	synthetic-fiber preparation and weaving:			
	manufacturing	90		viscose	80	60	
	cementing	80	25-30	celanese	80	70	
	surgical articles	75-90	25-30	nylon	80	50-60	
textiles	storage before manufacturing	60-75	40-50	tobacco	cigar and cigarette manufacturing	70-75	55-65
	laboratory (ASTM standard)	73.4	50		softening	90	85-88
	cotton:				stemming, stripping	75-85	75
	opening, picking	70-75	55-70		storage and preparation	78	70
	carding	83-87	50-55		conditioning	75	75
	drawing and roving	80	55-60		packing and shipping	75	60
	ring spinning:						

^a Listed conditions are typical; final design conditions are established by customer requirements.

maintained constant so as to minimize an increase in surface moisture films. If these surfaces are shipped or stored for extended intervals, protective coverings or coatings may be required.

The temperature and humidity should be maintained at, or below, comfort conditions, in order to minimize perspiration of the operator. Constant temperature and humidity may also be required in machine rooms to prevent the etching or corrosion of machine parts. Table 2 illustrates typical design conditions intended to minimize perspiration damage to machined surfaces. If perspiration causes only minor damage to the product and results in few rejects, then inside design conditions at 80°F and 40% rh are satisfactory. Where even small amounts of perspiration cause extreme damage to precision-machined parts and result in a high amount of rejects, inside design conditions of 70°F and 40% rh are recommended.

Table 2. Design Conditions to Minimize Perspiration
Damage in Precision Machining

Degree of perspiration damage	Conditions required for control	
	Dry-bulb, °F	Rh, %
moderate	80	40
large	75	40
extreme	70	40

3. Control of relative humidity is needed to maintain the strength, pliability, and regain of hygroscopic materials, such as textiles and paper. Humidity control may also be required in some applications to reduce the effect of static electricity.

4. Temperature and relative humidity may also have to be controlled in order to regulate the rate of chemical or biochemical reactions, such as the drying of varnishes, the application of sugar coatings, the preparation of synthetic fibers or other chemical compounds, or the fermentation of yeast.

AIR-CONDITIONING SURVEY

Estimating the air-conditioning load requires a comprehensive survey. All sources of heat to the conditioned space are carefully studied in order to obtain a realistic estimate of the heating and cooling loads. An analysis of the building structure is required to determine the heat gain from the sun, ie, orientation of the building, type of construction, surrounding structures, and reflective surfaces. People, lighting and machinery loads, and heat gains from chemical processes are evaluated, and extent of usage, hooded processes, and length of operations are considered. Outdoor air required for ventilation and for replacement of air exhausted through hoods is a heat load to the space.

The following factors must be taken into account in designing an air-conditioning system:

- A. Temperature and/or humidity to be maintained
 - 1. Allowable seasonal variations
 - 2. Permissible control tolerance
- B. Outdoor conditions to be assumed for design (not necessarily the extremes encountered)

- C. Architectural plans and details of building construction (if original plans are not available, the building must be measured carefully and details of construction must be determined by inspection)
 - 1. Orientation of the building with regard to the sun and to surrounding structures
 - 2. Zoning requirements based on sun effect, load concentrations, and differences in conditions required for various processes
- D. Sensible-heat gains
 - 1. Solar radiation and transmission through glass
 - a. Kind of glass
 - b. Shading devices
 - c. Reveals and overhangs
 - 2. Transmission, including sun effect, through walls and roofs
 - 3. Power
 - a. Usage factor
 - b. Percent loaded
 - 4. Lighting
 - a. Usage factor
 - b. Auxiliaries
 - 5. Miscellaneous (eg, ovens, exposed steam pipes, use of hoods)
 - 6. Temperature of product entering space
 - a. Product temperature above space temperature (resulting in a heat gain to the space)
 - b. Product temperature below space temperature (producing a credit to sensible-heat gain)
- E. Latent-heat gains
 - 1. Evaporation from wet surfaces due to process
 - 2. Migration of water vapor through building materials (especially important in low-dewpoint application)
 - 3. Water vapor from moist product
- F. Sensible- and latent-heat gains
 - 1. People
 - a. Degree of activity
 - b. Duration of occupancy
 - 2. Gas-burning equipment
 - a. Usage factor
 - b. Btu value of gas used
 - c. Use of hoods
 - 3. Heating equipment for evaporating water (capacity and usage factor)
 - 4. Chemical and biological reactions
 - 5. Infiltration of air
 - a. Frequency of door opening
 - b. Window cracks
 - c. Porosity of building structure
- G. Ventilation air
 - 1. For human occupancy
 - a. Number of people
 - b. Percent smoking

2. Toxic fume and smoke dilution
3. Odor dilution
4. Offsetting exhaust hood requirements

This information is required before the air-conditioning engineer can determine the load and complete the design of the basic equipment, the air-distribution system, and the automatic controls.

Air-Conditioning and Humidification Systems

AIR CONDITIONING

The most commonly known form of air conditioning is designed to produce an atmospheric environment most conducive to human efficiency and comfort. The range of temperatures and humidities suitable for this purpose, and for many industrial processes, is such that dehumidification is often required. In many industries, the processing of hygroscopic materials demands close control of air conditions the year round, and may also necessitate humidification. In most cases the spaces to be conditioned are occupied by people, so that outdoor air must be introduced for ventilation.

Systems of Air Conditioning. Figure 3 shows one of several types of air-conditioning systems. Outdoor air is drawn through a heating coil (preheater), and mixed with air returned from the conditioned space. The mixture is usually filtered before passing into a dehumidifier, which may be of several types. The air-washer type consists of a large number of spray nozzles, which atomize cold water in the air stream. Eliminators are provided to prevent carry-over of free moisture into the fan and duct system. Another form of dehumidifier may be of the "capillary" or "surface" type, in which chilled water is sprayed over devices designed to provide contact surface, and through which the air is passed. Such devices may be cells packed with glass filaments or other materials that provide large areas of contact surface. Both these types of dehumidifiers are referred to as "open circuit" type because of the actual contact between water and air. "Closed circuit" dehumidifiers are usually coils containing either chilled water or another cooling medium. Air is dehumidified by condensation on the cold surfaces. The choice between open or closed circuits depends upon the difficulty of cleaning and maintenance and upon the contamination of air or water. Where the air-conditioning equipment is located in remote areas; cleaning and maintenance are likely to be ignored; and atmospheric conditions create contaminated water, closed circuits are often used. Open circuits are particularly favored in processes where return air contains particles (such as lint from textiles) that can easily clog filters and coils. Sprayed coils and open circuits may be used for processes that give off odors that are soluble in water. However, in this instance, close control of water conditions must be maintained to minimize scale or corrosion.

Air leaves the dehumidifier nearly saturated, and passes through a reheater (steam, electric, or hot water) before being delivered by a fan and duct system to the conditioned space. Reheaters may be utilized for control in winter and also in summer, depending upon the particular requirements. Summer control is often provided by use of a bypass, which admits conditioned room air directly to the fan inlet in proportions governed by thermostats. Centrifugal fans are usually employed. In small systems up to approximately 40,000 cfm, multiple-fan wheels, mounted on a common shaft, may be used. Such systems usually fall into the "unitary" class, where the

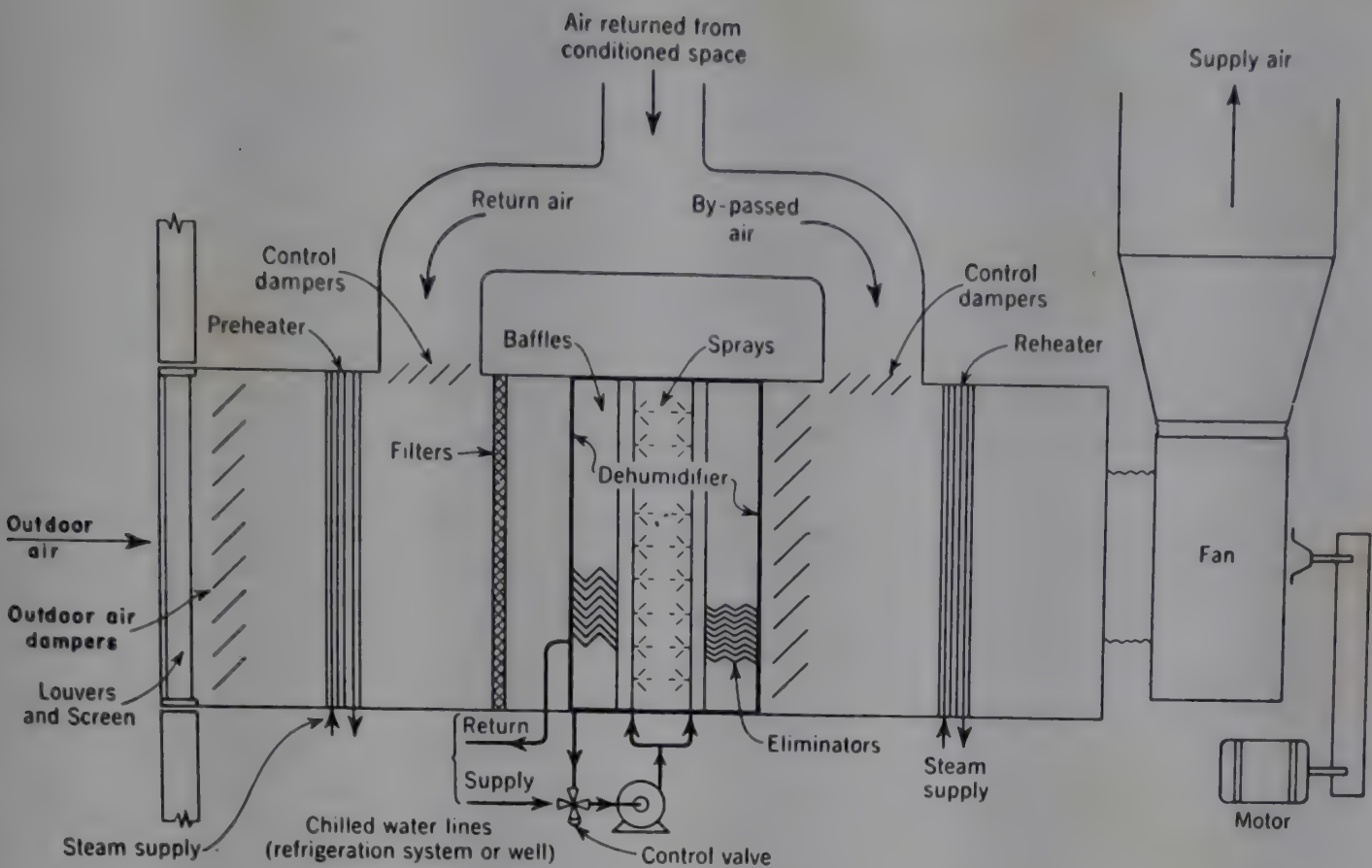


Fig. 3. Diagram of central-station system.

fan, heater, and dehumidifying-coil components are furnished in factory-assembled units. Spray- or capillary-type dehumidifiers may be utilized in field-assembled “central station”-type equipment with centrifugal blower fans or in the unitary-type system.

Methods of Refrigeration. The refrigerating effect for such systems may be provided by well water, if available at suitable temperatures and in sufficient quantity, or by refrigerating machines in conjunction with water chillers. Direct-expansion systems are frequently used where the condensed refrigerant is permitted to expand directly into a cooling coil over which the air is passed (see Refrigeration). Such systems usually employ reciprocating-type refrigerating machines in single or multiple units, depending upon the capacity required and the flexibility desired.

Winter Humidification. For winter operation, humidification is easily provided with either a central-station or unitary type of system. With the air-washer or capillary type, the entering air or the sprayed water may be heated, subject to control either by the dewpoint thermostat located in the discharge of the humidifier or by a humidistat located in the room. The spray-water heater may be of the conventional shell-and-tube type, in which steam is admitted to the shell, and the spray water is passed through the tubes and thus kept separate from the condensate. Where large capacities are required, the ejector type of water heater, wherein the steam is mixed with the water, may be used advantageously. The condensate is lost to the boiler, thus necessitating additional boiler-feed-water treatment, and there is the possibility of inadvertently adding odors to the air stream; on the other hand, the equipment is small, simple, and quick in response to control.

With the unitary-type systems, humidification may be provided by the release of live, low-pressure steam into the air stream or by the atomization of water produced by means of spray nozzles. Control is usually achieved by a humidistat. This

device throttles the spray water or turns it on and off as required. Pan-type humidifiers are employed where the required capacity is small. This type consists of a shallow pan containing water with a float-valve control; an electrically heated or steam-heated surface submerged in the water is usually controlled by a humidistat.

HUMIDIFICATION AND EVAPORATIVE COOLING

The range of temperatures and humidities required for industrial and chemical processes is frequently such that evaporative-cooling systems may be employed. These applications normally have a very high sensible-heat load and require inside-design relative humidities of 50% rh or higher, depending upon the particular operation.

The general arrangement of apparatus for a central-station, evaporative-cooling installation is similar to that shown in Figure 3, except that spray water is continuously recirculated without chilling. When maximum cooling effect is required, all outdoor air is drawn into the spray chamber, where its moisture content is increased close to the saturation point. No external transfer of heat occurs; the saturation takes place adiabatically. The wet-bulb temperature and enthalpy of the entering air remain for all practical purposes the same, but the sensible heat of the air is transformed into latent heat to provide the heat of evaporation of the water taken up by the air. An example showing how the psychrometric chart may be used to plot the conditions (as locants of dry- and wet-bulb temperatures) that will produce a specified degree of cooling and humidification is shown in Figure 1. If, on the other hand, the conditions are given, the chart will show the resulting temperature and relative humidity.

The sensible-heat factor (also see Fig. 1) is used with sensible-cooling and with cooling and dehumidification processes. With this scale, the design engineer knowing the sensible and latent heat to be removed and the dry- and wet-bulb temperatures of either the air entering or the air leaving the apparatus may plot his particular cooling process, as follows: (1) He calculates the sensible-heat factor; (2) plots a line from the calculated sensible-heat factor on the scale of the psychrometric chart to the alignment circle (at 80°F dry-bulb and 50% rh); and (3) draws the actual sensible-heat-factor process line by plotting a line through the points indicating the actual conditions of the entering or leaving air and parallel to the base line in step (2). This provides the engineer with a visual representation of his particular cooling process.

A thermostat in the spray chamber controls dampers that mix outdoor air and air returned from the conditioned space, so that the dewpoint may be held at a constant level during cool weather. Admission of steam to a spray-water heater is also controlled by this thermostat, so that the dewpoint may be maintained in cold weather. Air from the washer is passed through reheaters and is then discharged into the room by a system of ducts and diffusing outlets. This system primarily controls humidity, since the room temperature is permitted to rise when the wet-bulb temperature of the outdoor air exceeds the desired room dewpoint. To illustrate, an application may require 65% relative humidity. The temperature in the room would be approximately 89°F with outdoor conditions of 95°F dry-bulb and 75°F wet-bulb. When the outdoor wet-bulb is lower than 75°F, the indoor dry-bulb may be correspondingly lower. If it is desired to hold the dry-bulb temperature at a constant level, it is necessary to provide a means of removing heat in the washer, in which case the system is similar to the central-station type shown in Figure 3.

Areas that require only humidity control, and where heat gains are small, can frequently utilize atomizing spray nozzles alone without mechanical ventilation. Such systems are frequently installed in warehouses for tobacco and paper storage. Atomizing heads are distributed over the area, and connected with compressed-air and water lines. Water is broken up into fine particles by a jet of compressed air, and is quickly evaporated into the room air. The humidifying rate is controlled by a hygrostat that turns the nozzles on and off as required. If there are internal-heat loads in the space, the resulting temperatures may become intolerable for human occupancy unless sufficient outdoor air is introduced. Reliance is often placed on open windows or gravity ventilators, but the temperatures are seldom comparable with those produced by the central-station, evaporative-cooling systems, unless equivalent quantities of outdoor air are introduced through mechanical ventilation.

For humidities of 65% and higher, "combination" systems are frequently installed. In these systems atomizing spray nozzles are placed in front of the outlets of a central-station, air-washer installation. Such systems produce room temperatures that may be as much as five degrees higher than the systems utilizing only the air washer, depending upon the ratio of atomized water to the air supplied. Compared with the 100% central-station system for a given relative humidity, a combination system has a lower initial cost, and requires less space for apparatus and ducts.

CHEMICAL NEUTRALIZATION

Spray-type washers are used extensively for removal or neutralization of noxious components from large volumes of gas or air. Appropriate reagents (chemical neutralizers) are sprayed into the washer to purify the air or gases by neutralization. For example, sodium hydroxide solution is used if the air contains acid gases. The solution must be continuously reconcentrated and the precipitated salts removed. The contact efficiency of such washers is high, and the simple construction provides easy maintenance and constant efficiency. (See Gas cleaning.)

LOW-HUMIDITY SYSTEMS

Some industrial processes require low humidities, and when the dewpoints required at the apparatus approach or fall below the freezing point, dehumidification can often be better produced with dehydration equipment. This equipment permits the use of solid sorbents, such as silica gel and activated alumina, or of liquid sorbents, such as lithium chloride brine and triethylene glycol. (See Driers.)

Dehydration of air by liquid or solid sorbents is for all practical purposes adiabatic, and the enthalpy of the air remains essentially the same. The air leaving the dehydrator, therefore, is at a higher dry-bulb temperature than the air entering. It is necessary to provide an aftercooler for sensible-heat removal if lower room dry-bulb temperatures are required. Chemical dehydration (as opposed to simultaneous cooling and dehumidifying) is most favorable when (1) a cheap source of sufficiently cool water is available, (2) the cost of gas or steam for reactivation is low, and (3) a large portion of the load is latent heat.

Solid-sorbent processes utilize the property of certain solid substances to adsorb water vapor. As the material fills with water, the attraction becomes balanced by the internal vapor pressure until an equilibrium condition is attained. The total weight of water that can be adsorbed is a function of the temperature of the material and the

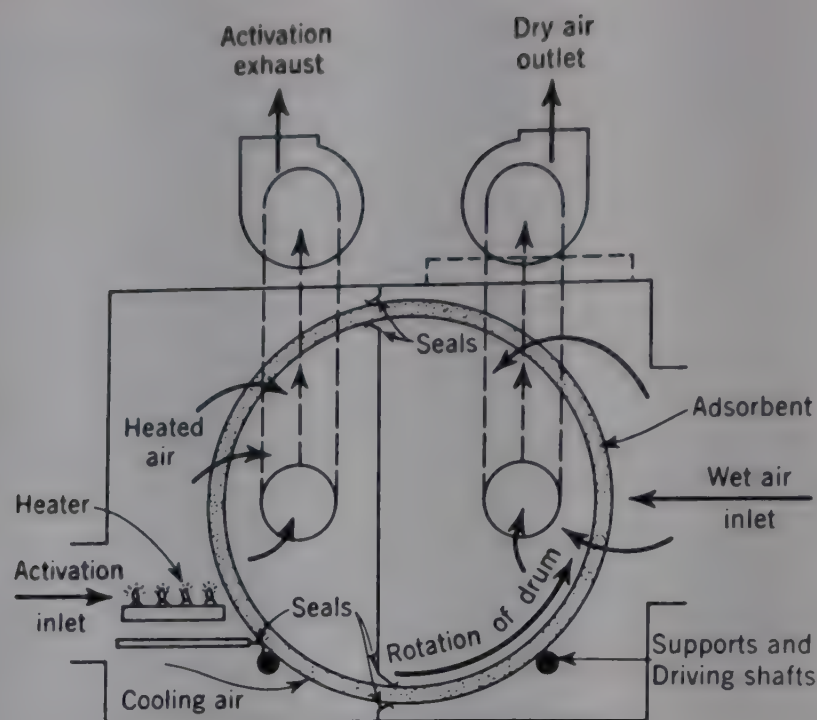


Fig. 4. Bryant continuous rotary dehumidifier (dehydrator). Courtesy Bryant Manufacturing Company.

relative humidity of the air. When the temperature is raised or the humidity lowered, moisture is driven out. The solid sorbents are silica (qv) and alumina (qv under Aluminum compounds).

These substances are utilized in either intermittent or continuous equipment. The air to be dehumidified is passed through the adsorber bed during the dehydration cycle. After adsorption of moisture the rate of removal becomes impaired and the bed is subjected to reactivation, during which moisture is driven off by direct firing or hot air. When reactivation is complete, the bed is cooled by outdoor air, to remove the residual activation heat. The moisture-laden air from the reactivation, and the air from the cooling part of the cycle, are discharged out-of-doors. In the intermittent process, two beds are operated to afford continuity of operation, one being on the dehydration cycle at the time the other one is reactivating and purging; dampers effect the switch-over. With the continuous type, material may be carried at the periphery of a revolving drum and subjected successively to the dehydration, reactivation, and cooling phases, or it may be held stationary while a rotating port valve subjects it to the three cycle phases. Figure 4 shows the schematic flow diagram for a typical rotary dehydrator.

Liquid sorbents may also be used for low-humidity systems. The vapor pressure exerted by water depends on the temperature, and the air remaining in contact with the water or water vapor absorbs moisture by evaporation until its vapor pressure exactly equals that of the water, at which time equilibrium is reached. Many salts in aqueous solution have the property of markedly reducing the vapor tension exerted by the solution below that of pure water. Such a solution, if of proper strength, causes moisture to condense from the air even though the solution temperature is much higher than that corresponding to the dewpoint of the air. Brines of calcium chloride, lithium chloride, lithium bromide, and calcium bromide are used, either singly or in combination; triethylene glycol, and to a lesser extent diethylene glycol and ethylene glycol, are also used (see Calcium compounds; Carbon; Glycols; Lithium compounds). The concentrated mixtures of the glycols with water are also referred to

as "brines," though they do not have the corrosive properties characteristic of the halide brines. Besides having favorable vapor-pressure characteristics, the brine used should not have a solidification curve too near the working range, must be odorless, relatively noncorrosive, chemically stable, and reasonable in cost. The most serious application hazards are corrosion, due to contamination of the brine, and carry-over from equipment into the room, which is not tolerable even if extremely minute. Equipment is available that overcomes these faults.

Figure 5 shows the operation of the principles outlined above. The air to be dried contacts the brine, either by spray or wetted surface; as a result, the moisture content of air is reduced, the temperature of both brine and air is increased (by heat of condensation and dilution), and the concentration of brine is decreased by the amount

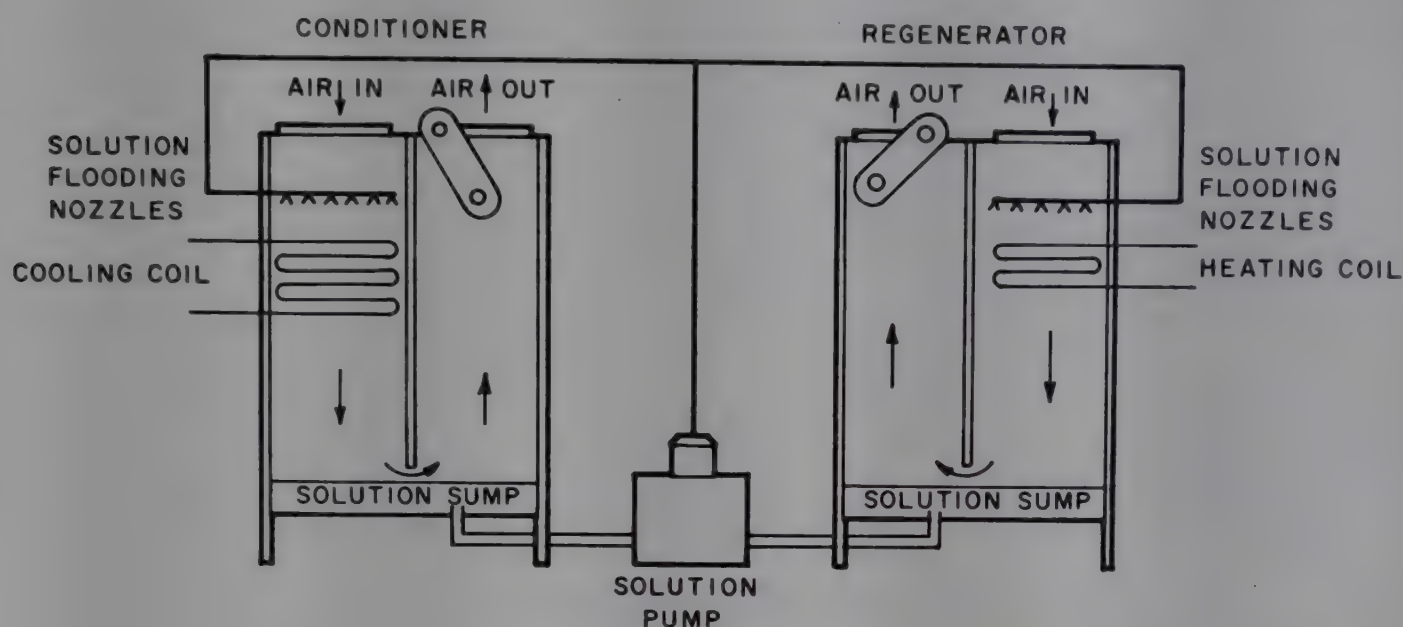


Fig. 5. Typical liquid-sorbent dehydrator.

of water condensed. For reconcentration, the brine is heated and water is either boiled off or evaporated at a lower temperature in a reconcentrator. The solution is then cooled, usually in a brine-water interchanger, to a temperature suitable for dehumidification, and the cycle is repeated. Several variations of this procedure may be employed in the brine circuiting, and additional heat exchangers may be used. The brine and air may be cooled in the dehydrator simultaneously to achieve the required dry-bulb temperature of the supply air, and to reduce brine temperature so as to permit the lowest possible vapor pressure. Since brines can be pumped, there is no problem in making this process continuous.

CONTROL OF THE AIR-CONDITIONING SYSTEM

Automatic control of the air-conditioning system is required to compensate for variations of heat gains resulting from movement of the sun, change in outdoor temperatures, differences in loadings from loadings applying to machinery and chemical processes. Such variations of load seldom take place simultaneously in all areas; therefore it is necessary in most applications to zone the air distribution system. Room conditions in one area are controlled independently of conditions in other areas by use of reheaters, volume dampers, recirculation fans, or other means.

Table 3. Summary of Various Methods of Controlling the Condition of Air in an Enclosure

Control method	Room condition ^a					
	Temper- ature	Relative humidity	Absolute humidity	Dust	Odor	Toxic gases
coils or plates						
heating surface	+	-				
cooling surface	-	+	-			
air washers						
chemical neutralizer	-	+	+	-	-	-
recirculating-water spray	-	+	+	-	(-)	(-)
cold-water spray	-	±	±	-	(-)	(-)
warm-water spray	±	+	+	-	(-)	(-)
room sprayers						
steam spray	+	+	+			
atomizing water spray	-	+	+			
dehydrators						
silica gel	+	-	-			
activated alumina	+	-	-			
lithium chloride	+	±	±			
triethylene glycol	+	±	±			
calcium chloride	+	-	-			
air cleaners						
mechanical filters				-		
electrostatic precipitators				-	(-)	(-)
centrifugal collectors				-		
activated carbon					-	-

^a Increase: + Decrease: - Slight decrease: (-) Increase and decrease: ±

Uses of Air Conditioning in Industry

Many industrial processes require accurate environmental control for physical or chemical reactions, while others demand controlled conditions in order to attain necessary uniformity of quality and dimensional stability. Among the functions of air conditioning in modern industry are the following: (1) to control certain chemical reactions and processes that are affected by atmospheric conditions; (2) to control the rate of biochemical reactions; (3) to control quality, uniformity, and standardization; (4) to control such factors as rate of crystallization and size of crystals; (5) to control regain or product moisture content; (6) to prevent deliquescence, lumping, and caking of hygroscopic materials; (7) to control expansion and contraction of machines and products; (8) to control physical, chemical, and biological cleanliness; (9) to minimize effect of static electricity (see also Antistatic agents); (10) to control odors and fumes; (11) to control conditions in storage and packaging; (12) to control quality of painted and lacquered finishes; (13) to simulate stratosphere or space conditions; and (14) to increase the productivity of workers.

A few of the major industries in which air conditioning is used extensively as well as some of the significant advantages of controlled atmospheric conditions are indicated below.

SYNTHETIC FIBERS

In the synthetic-textile industry, represented by rayon (qv) and nylon (see Polyamides), air conditioning is used to achieve uniform quality and viscosity for spinning; to control the rate of reaction and coagulation; to control toxic fumes and evaporation

from acid baths; to control (by prevention of stretching) the winding of wet threads; to control regain; and to prevent crystal formation on threads and machines. Because of toxic fumes in some rayon processes, air conditioning with a large amount of outdoor air and supplemented by extensive exhaust is a hygienic necessity. In the mechanical handling of the finished synthetic yarns, in throwing, weaving, and knitting operations, air conditioning is necessary for quality and production control. (See also Textile technology.)

One typical problem encountered in a plant manufacturing viscose rayon is the prevention of condensation on sodium cellulose "crumbs" and on the shredding machinery. Refrigerated water or brine is used for jacketing the machines to remove the heat of chemical reaction and the heat from motors driving the shredders. The crumbs are chilled in the process and require handling the air at a dewpoint not above 50°F to avoid troublesome condensation on both the material and machine surfaces. The dry-bulb is held at approximately 65°F, and the air-conditioning apparatus consists of a central-station system having a chilled-water spray dehumidifier with fans, reheaters, and controls, resembling those shown in Figure 3. A similar system is used in the churn room, where the white crumbs are treated with carbon disulfide to form cellulose xanthate, or "orange crumbs." A dry-bulb temperature of 75–80°F is required winter and summer. Large quantities of outdoor air are needed to dilute and remove the explosive and toxic fumes. The heat of the reaction in which the viscose rayon is produced by treatment of the cellulose xanthate with sodium hydroxide is removed by brine- or water-jacket cooling, and the viscose solution is ripened in a closely controlled, constant-temperature room to assure the proper viscosity for spinning. In addition, it is necessary to dilute and remove the acid fumes generated in the spinning room, which is held at 80–85°F dry-bulb and 75–80% relative humidity to prevent crystal formation on the spun filament. Central-station spray-type apparatus is also employed for this room. Another use for air conditioning is in the succeeding processes of washing, bleaching, and drying, and in final sorting and grading.

PHARMACEUTICALS AND BIOLOGICALS

Air conditioning is an important processing requirement in the production of many pharmaceutical materials, as in the manufacture of pills and capsules and in the packaging of the finished product, in order to maintain constancy in formula, quality, and measurements. It helps to achieve constant production rates, cleanliness, and purity of product; to prevent lumping, caking, and sticking; to reduce diffusion of material into the air; to remove noxious fumes and gases; and to produce the desired polished finish on coated pills (see Pharmaceuticals).

An example typical of air conditioning in this industry is a system used in a well-known pharmaceutical plant that provides the proper environment for capsule filling. In this process, low relative humidity is required to prevent lumping of the hygroscopic material. Close control of temperature and humidity is needed for uniform quality and filling of the capsules as the gelatin capsules, for example, become soft and sticky at too high a temperature and humidity, and brittle at a low temperature and humidity. The space served by the system consists of several rooms of vapor tight construction, to minimize the seepage of moisture due to the fairly great difference in vapor pressure between the outdoor air and the conditioned space. The conditions maintained year-round in the spaces are 80°F dry-bulb and 20% relative humidity (35.2°F dewpoint, 30 grains per pound of dry air). For this application, a silica-gel

dehydration system is used because the low dewpoint would have required lower-than-freezing spray- or coil-surface temperatures. The air-conditioning system is schematically shown in the flow diagram in Figure 6. The air cycle is as follows: Outdoor air is mixed with a portion of return air from the conditioned space and drawn through a bed of silica gel, which is continuously reactivated by direct-fired gas heating. Dry air is discharged from the dehydrator, cooled by city water in an aftercooler coil, mixed with return air, filtered, and drawn through sensible-heat cooling coils (direct expansion of Refrigerant-12 (dichlorodifluoromethane) from a reciprocating, condensing unit), and then discharged by means of a supply-air fan to the various spaces. Each space has its own reheater, which is used to maintain constant dry-bulb conditions year-round. Return air is taken from each space and drawn through filters by a return-air fan, which delivers part of the air to the wet-air inlet of the dehydrator and recirculates the balance to the sensible-heat cooling coil.

RUBBER

In the rubber industry, air conditioning provides uniform performance in drying and shortens the drying period, controls oxidation, eliminates blisters in dipping operations, preserves tensile strength, minimizes explosion hazards from static electricity, and reduces the concentration of toxic fumes. (See Rubber compounding and fabrication.)

PHOTOGRAPHIC MATERIALS

Air conditioning is an essential element in the processing of photographic materials, in controlling the regain of film, in minimizing static-electricity discharge, thus reducing fire hazard and preventing fogging and streaking, in assuring dust-free air, and in providing ideal conditions for packaging and storage, thereby reducing production losses. Close control of temperature, humidity, cleanliness, and ventilation is a practical and essential necessity. (See Photography.)

EXPLOSIVES

The munitions industry employs air conditioning to control uniformity in the manufacture and loading of the various explosive mixtures, to control drying and moisture content, to minimize static-electricity discharges and reduce the hazards of fire and explosion, to remove and neutralize toxic fumes, to remove and recover dust or solvents from manufacturing or loading processes, and to provide proper atmospheric conditions for the storage of raw materials or finished product. (See Explosives.)

BREWERIES

Air conditioning and the extensive use of refrigeration are necessary to provide controlled temperature in wort cooling, fermentation, and storage and final packaging of the finished beer. Sanitation and removal of carbon dioxide are important aspects of this application. (See Beer.)

FOOD PROCESSING

Air conditioning, including drying and freezing, has many applications in connection with food processing. Examples are food dehydration, blast freezing, smoke

houses, storage facilities, canned and dried foods, frozen foods, meat packing, chewing gum manufacturing, concentrated fruit juices, and hard and chocolate candy. (See Confectionery; Food.)

METAL INDUSTRY

Air conditioning plays an important part in cupola and blast furnaces and in Bessemer converters. It either supplies air of proper moisture content or increases worker comfort (for example, in crane cabs, pulpits, or other individual "hot" operating spots). This is accomplished by individual or group spot cooling. Controlled temperature and humidity conditions are necessary for powder metallurgy, a low temperature in metal fitting, and humidity control in metal finishing, to eliminate perspiration stains, etching, and rust.

CERAMICS

The drying of ceramic products before firing is controlled by air conditioning, to standardize form and dimension, establish uniform drying and a controlled rate of drying, and to prevent setting up strains that may otherwise cause cracking and crazing during firing. (See Ceramic industries.)

LABORATORIES

Wide ranges of temperature from approximately -170 – 250°F , of humidity from 5–95%, of atmospheric pressures to a high altitude—these and even special ambient conditions are not unusual for test chambers and in some instances even for complete laboratories. Requirements may be either to maintain constant conditions or to alternate high and low temperatures in conjunction with high and low humidities. Test facilities may be designed to test materials and products—determining specifications and standards, and testing for compliance with these specifications and standards—and to determine environmental standards. It is also anticipated that temperatures of -300°F will be required to simulate space travel.

Approximate Cost of Air Conditioning

The initial cost of air conditioning varies throughout a wide range. It depends on many factors, such as the room conditions to be maintained, the load imposed, the building construction, and the type system used to provide the desired conditions. The following figures, which refer to 1961 costs, are rough approximations and are intended to give some indication of the cost for some applications in the United States only. The initial costs are exclusive of building construction and electrical wiring, items which may add 5–200% and which must be evaluated separately. The annual operating costs are based upon 15-year amortization at 5% interest, and do not include taxes and insurance.

For installations designed for office workers in a building having normal windows, 3–5 watts of lighting and power per sq ft floor area, one person per 80–100 sq ft, ventilation air at the rate of 10–25 cfm per person, and room design conditions of 78°F dry-bulb and 45% rh, the initial cost is \$2–\$10 per sq ft, \$600–\$1500 per ton of refrigeration; annual operating cost, \$0.48–\$1.25 per sq ft.

For applications requiring a low dewpoint and having 5 watts per sq ft, ventilation air at the rate of 10–25 cfm per person and room conditions of 70 – 75°F dry-bulb and 20–45% rh, the initial cost is \$8–\$11 per sq ft, \$2.40–\$3.00 per cfm of supply air.

VOLUME 1, Page 501
Alcoholic Beverages, Distilled

The article "Alcoholic Beverages, Distilled" was written by George S. Packowski of Joseph E. Seagram & Sons, Inc. As in the case of all other articles in the Encyclopedia, this article reflects to some extent the opinion of the author and the company he represents.

Some of our readers, in particular The Bourbon Institute, feel that the article does not properly represent the attitude of a large segment of the U.S. distilling industry with regard to the discussion of neutral spirits.

We are giving herewith the official definition of neutral spirits as stated in "Federal Labeling and Advertising of Distilled Spirits," 27 C.F.R., Part 5, Section 5.21, The Standards of Identity (a) Class 1.

"Neutral spirits or 'alcohol' are distilled spirits distilled from any material at or above 190° proof, whether or not such proof is subsequently reduced."

Costs of evaporative cooling systems vary widely. The air quantity and cost both vary directly with the sensible load. For a typical application—lighting, 1.5–2.0 watts per sq ft; power, 30–40 watts per sq ft; people, 500–1000 sq ft per person; room conditions, 85–95°F dry-bulb; and 60% rh—the initial cost for a central-station, evaporative-cooling system is \$2.70–\$3.30 per sq ft; \$0.24–\$0.33 per cfm supply air for all-air systems; and \$0.33–\$0.66 for combination systems.

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R. ELSEA AND R. C. TERWILLIGER, JR.
Carrier Air Conditioning Company,
a Division of Carrier Corporation

AIR, LIQUID. See Cryogenics.

ALCOHOLATES. See Alkoxides, metal.

ALCOHOLIC BEVERAGES, DISTILLED

History

In the Old World. The origins of distilling are veiled in antiquity, even though the history of distilled spirits is much shorter than that of fermented liquors. Scientists have unearthed pottery in Mesopotamia depicting fermentation scenes dating back to 4200 BC. A small wooden model of a brewery dating back to 2000 BC is on display at the Metropolitan Museum of Art in New York City. By 800 AD monks were producing substantial amounts of fermented liquors in Europe.

Insofar as recorded history is concerned, Aristotle mentions purifying sea water by evaporation and a wine which produces a “spirit.” But the first real distiller was probably a first or second century Greek-Egyptian alchemist who, in an attempt

to transmute base metal into gold, boiled some wine in a crude still. The discovery of "ardent" spirits which resulted from this effort was looked upon with awe. It was hoarded and secreted and made known only to a select few for many centuries.

Historians believe that the knowledge of distillation came from the Egyptians who had been interested in alchemy since before the time of Christ. At a later time the Arabians gained this knowledge from the Egyptians. The European countries were introduced to distillation either through Spain about 1150 AD, or from the Crusaders who learned about it from the Moslems in the 12th and 13th centuries. There is reason to believe that distilled spirits were possibly known in Ireland and Scotland prior to the 12th century AD, but actually it was not until then that there is a recorded history of distilled spirits in Europe. The first written evidence is in the description by Master Salernus who died in 1167 AD. However, for another three centuries distilled spirits were regarded only as a rare and costly medicine called "Aqua Vitae," the water of life.

The first treatise on distillation was written by a French chemist, Arnold de Villeneuve, sometime before 1311, and the book was printed in 1478 in Venice. A Spaniard, Raymond Lully, was also instrumental in spreading the knowledge of distillation through Europe in the late 13th century. "Liber de Arte Distillandi," by Hieronimus Brunswick, a well-known author of medical works, was printed in 1500 in Strassburg. An even more comprehensive book by Ryff, another medical author, appeared in 1556 in Frankfurt am Main. Both works contain elaborate chapters on herbs and their distillates with indications of their uses as medicines.

The new art of distillation was first carried out in monasteries since churchmen were the only scholars capable of reading and understanding the treatises on distillation. Gradually, the knowledge of "Aqua Vitae" spread widely and during the 16th and 17th centuries the production of distilled spirits became a full-scale industry. The rise in the popularity of distilled spirits in Europe came during this same era and may best be traced through court records.

The word "whisky" comes from the Gaelic word "uisge-beatha" or "usquebaugh," as the Irish called it, meaning the "water of life." Usquebaugh, supposedly the Celtic form of whisky, was actually a cordial, made with aniseed, cloves, nutmeg, ginger, caraway seeds, raisins, licorice, sugar, and saffron. The real whisky of the Irish was called "potheen," reputedly a very formidable drink, full of heavy-bodied flavors resulting from simple distillations.

The early methods of distillation utilized the alembic, a simple closed container for the liquid, to which heat was applied. The vapors were transferred through a tube to a separate cooling chamber in which they were condensed to a liquid. Alembics made of copper, iron, or tin were preferred. Other metals were said to have an adverse effect on the distillate. Occasionally, glass and potter's earth were used. From this developed stills consisting of clay or brick fireboxes into which the copper pots of the still were fitted. To the body or cucurbit containing the fermented mixture, direct heat was applied, and the vapors rose into the head, passed through a pipe called the "crane neck" to the worm tub, where a copper coil was immersed in a barrel of cool water. Variations of this technique with improvements, of course, resulted in pot stills, some of which are still in use as primary systems in the production of malt whiskies, notably in Scotland, and of brandies, in France.

During the latter part of the 18th century, great strides were made in the development of distillation equipment. The major credit for this must be given to the French.

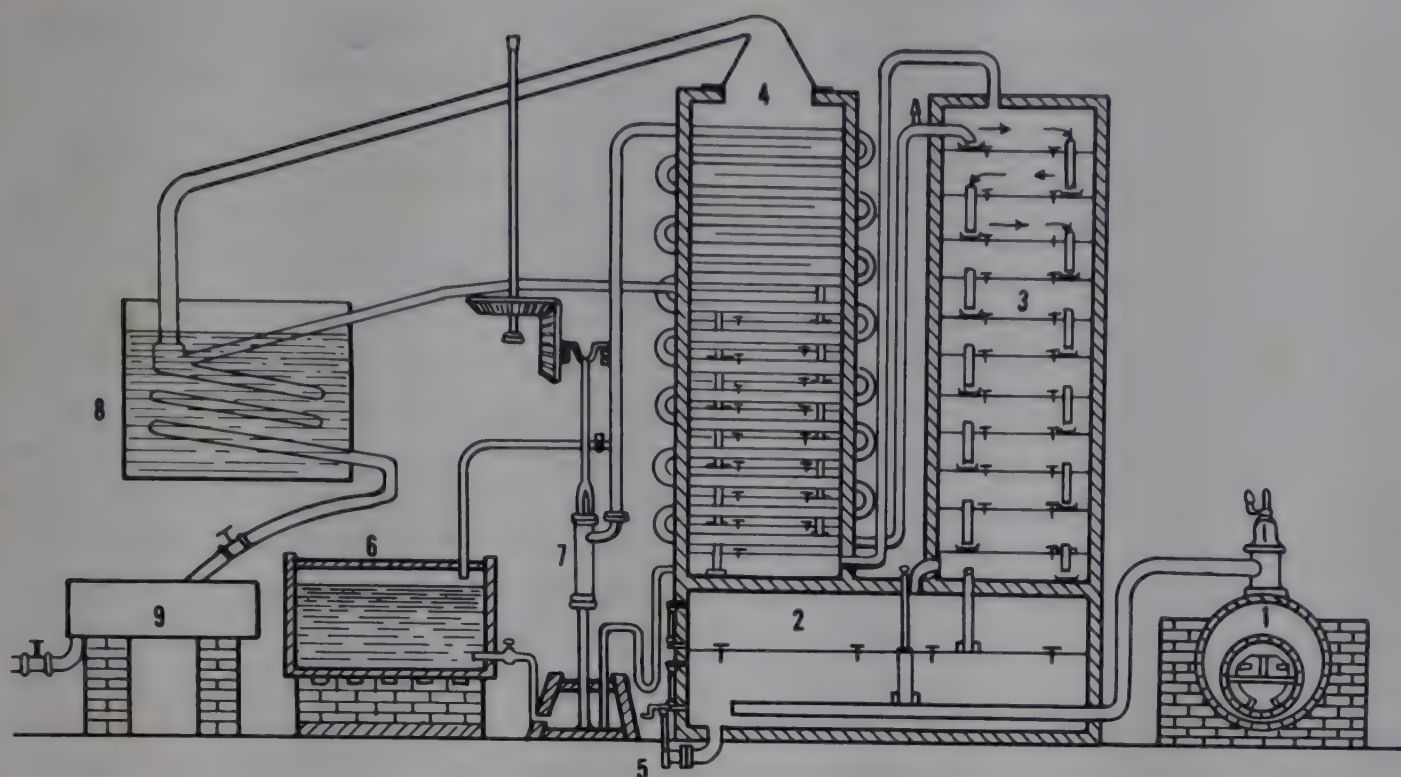


Fig. 1. Coffey still. 1. Boiler. 2. Spent mash chamber. 3. Stripping column (analyzer). 4. Rectifying column. 5. Residual mash (stillage) outlet. 6. Fermented mash (feed). 7. Feed pump. 8. Condenser. 9. Product tank.

Since brandy (from fruit) was the principal distillate in France, the French had an advantage over the British and Germans, both of whom were hampered by the thick mashes from grains. Argand invented the preheater. In 1801, Edouard Adam designed the prototype of a charge still. He used "egg-shaped" vessels to hold the alcoholic liquid through which vapors from the kettle passed successively to the condenser. In 1805, Berard obtained a patent on a still using the principle of partial condensation to achieve vapor enrichment. Another Frenchman, Cellier-Blumenthal, obtained a patent in 1813 on a continuous still which was later modified by Derosne and Coil. Before this, an Englishman, Wyatt, was granted a patent in the use of steam for heating stills and a trial was made with a still jacketed for steam heating. It was rejected by the Bureau of Excise on the grounds that it would facilitate illicit operations. Nevertheless, Aenest Coffey, in Dublin, in 1830 took advantage of this method of heating when he developed his continuous still. The Coffey still (see Fig. 1) is composed of two columns; in one the fermented mash is stripped of its alcohol, and in the other the vapors are rectified to a high proof (94–96%). With the invention of the Coffey still, almost all of the fundamentals of distillation had been recognized and incorporated into still design. Later developments, although of great importance, do not differ fundamentally from the stills of Cellier-Blumenthal and Coffey.

In America. The early history of distillation in this country is almost as undocumented as that of its beginning elsewhere. No one knows who made the first rum, Colonial New England's most important product; no one knows when or where the first rye whisky was made or with any certainty the first bourbon maker in Kentucky. In America there is a possibility the Indians might have known about distillation. All Indian tribes had fermented drinks, some from maple syrup, some from corn, some from ground acorns, chestnuts, and chinquapins. Christopher Columbus reported an Indian drink made from the marrow of maguey. The fermented sap of

maguëy makes pulque—distilled pulque becomes mescal. Whether or not Columbus tasted mescal is conjectural. However, along with the Spanish and Portuguese came the still.

The first recorded beverage spirits made from grains in the United States of America were distilled on Staten Island in 1640 by William Kieft, the Director General of the Dutch Colony of New Netherland. Wilhelm Hendricksen, in charge of the still, utilized both corn and rye as basic materials.

During the early days of the new colonies, fermented beverages made from sugar-bearing fruits and vegetables were very popular. Pumpkins, maple sugar, parsnips, peaches, pears, apples, currants, grapes, and elderberries provided a ready source of materials. The more aristocratic colonists preferred imported wines. However, the 18th century colonial drinking customs changed to distilled drinks, especially rum. Rum was made in Barbados as early as 1650. In America, the earliest reference is in the records of the General Court of Massachusetts in May, 1657. By 1750, there were sixty-three distilleries. One of the first acts of the Continental Congress was to establish a ration of rum for soldiers and sailors. Brandy, which had been made in America as early as 1650, and gin, which was very popular with the poorer classes in England, never had the popular appeal of rum in this country. Nevertheless, rum was not a native drink since it was necessary to import the raw materials.

With the decline of the "three-cornered" trade, the advent of revolution, and the movement of settlers from the coastal areas into the hinterland, the rum industry slowly declined. To replace molasses, it was natural for the Americans to turn to rye, which was a successful crop in Pennsylvania and Maryland, and to corn, which flourished in the South and West. Many Germans, who brought with them the knowledge of distillation from Europe, most likely began to distill spirits as soon as they became settled. George Washington is credited with the making of rye whisky in America. His distillery had an excellent reputation for making fine liquor under the supervision of James Anderson, a Scotsman. In 1798, the record reveals that Washington's net profit was £83 with an inventory of 155 gallons still on hand.

Canada's first distillery was started at Quebec City in 1769 producing rum from molasses. The making of whisky did not develop until the 19th century. By 1850 there were some 200 distilleries operating in Ontario alone. Today there are only 21, of which two, Joseph E. Seagram & Sons, Ltd., and Hiram Walker & Sons, Ltd., have been in business continuously since 1857 and 1858, respectively.

The Whisky Rebellion (1791) and Alexander Hamilton's foray that provided the decision that a member state must submit to central authority, resulted in the rise of Kentucky as the greatest whisky-producing state in the Union. Kentucky, which had achieved statehood in 1792 with over 70,000 inhabitants, many of them Scotch-Irish and German immigrants continuing their farmer-distiller background, had in 1810, 2,000 stills out of 14,000 in the United States producing well over two million gallons of whisky annually.

As many counties of Kentucky claim the first production of bourbon as Greek cities quarrel over the birthplace of Homer. However, it is generally agreed that the first bourbon whisky—"genuine, old-fashioned, handmade, sour-mash bourbon"—was made by a Baptist minister, the Reverend Elijah Craig, in 1789 at Georgetown in Scott County. At that time Scott County was part of Bourbon County, from which Elijah Craig's corn whisky got its name. Bourbon, Lincoln, and Jefferson Counties were the original Virginia counties that made up the Kentucky territory. In order to

distinguish this corn whisky from Pennsylvania rye, the whisky of the West was called Kentucky bourbon, with a mashing formula of at least 51% corn grains. Up to 1865, few Kentucky distilleries produced more than 1,000 barrels per year. Most of them were small, producing only 50 to 500 barrels of whisky.

The method of making whisky, with the exception of malt preparation, was in most respects similar to that used in Scotland and Ireland for hundreds of years. Ground corn and rye meal were scalded in tubs somewhat larger than barrels, stirred with paddles, and allowed to cool and sour overnight. Then malt made from rye or corn was added for conversion of the starch to a fermentable grain sugar. Yeast was added and the mash allowed to ferment from 72–96 hours. A simple, single-chambered copper still was used to separate the spirits from the mash. When redistilled, the product was called “double distilled.” In 1819, New Orleans received some 200,000 gallons per month of this type of Kentucky product. By the time it had floated down the Ohio and Mississippi on flatboats, the hot sun and boat movement had “aged” it.

Before the Civil War, not much attention was paid to ageing, even though it was recognized that whisky left in charred oak barrels took on a golden color and some mellowness. Originally, whisky was sold in its natural white state or artificially colored to resemble the amber glint of brandy. No one bothered with brand names—whisky was whisky, as everyone knew—and not too much was made of the wide variation in palatability. The hunter or riverman who indulged himself with raw white whisky was not particular about quality.

After the Civil War, the rise in taxes made storage in bond desirable. Many family names, always important in Kentucky lore, now became associated with distinctive whiskies. As the industry grew, it engaged in bitter controversy over what was whisky. As a result, in 1909 during President Taft’s administration, whisky was finally defined as any volatile liquor distilled from grain, and standards of identity based upon current manufacturing processes for various whisky types—rye, bourbon, etc—were established (1). Before the Taft decision few brands were nationally known. The incentive to advertise quality was destroyed by the flagrant exploitation of markets by local labels making fantastic claims which were left unchecked until the passage of the Pure Food and Drug Act of 1906. The new regulations also required labels to tell the process and materials of manufacture. The way was opened to national advertising. By 1920 when Prohibition began, blended whiskies comprised 70% of the whisky market. The 18th Amendment to the Constitution of the United States, which went into effect Jan. 16, 1920, halted the growth of a powerful industry.

Prohibition brought with it evils that were greater than those it was designed to prevent. During Prohibition, consumption of spirits increased from 140 million to 200 million gallons annually. Much of the drinking, of course, was reckless and dangerous, and the graciousness and dignity of sensible social drinking was, in a large measure, destroyed by the frantic defiance of a bad law. In 1930 the Director of the Prohibition Enforcement Bureau estimated that the production of moonshine was more than 800 million gallons a year, most of which went into synthetic gins and semilethal cocktails. On December 5, 1933, the 21st Amendment to the Constitution was ratified by the 36th state, Utah, and the great industry, which had been paralyzed by years of inaction, slowly awoke to the new developments in bacteriology, chemistry, engineering, sanitation, and research. Many of the small producers were absorbed by the major organizations. This provided capital for the necessary new equipment and the investment in inventory, and the industry faced the rehabilitation of social drinking in the U.S.

While per capita consumption continued to decline (it was 2.71 gallons in 1864, 1.71 in 1922-1930, and only 1.31 in 1960), the growth in population accounted for an increase in total consumption from 145 million wine gallons (see p. 521) of distilled beverage spirits in 1940, to 190 million in 1950, and to over 234 million in 1960. With emphasis on quality, brand names with nationwide distribution became popular. The advent of World War II again disrupted the industry, which offered its facilities to the Government for war alcohol production, even before the United States entry into the war. From Pearl Harbor to V-J Day, 750 million gallons of 190° alcohol was produced for the war program by registered distillers, who during peak production in 1944, utilized 127 normal beverage plants.

Since whisky production was restricted during the War, except for two very short periods, some distillers had to resort to redistillation of precious whisky reserves in order to maintain their prewar standards of quality, in addition, of course, to reducing their shipments. After 1951, with depleted inventories replaced, the industry turned again to the marketing of American whiskies, featuring fine quality under nationally advertised brand names.

TAXATION, GOVERNMENT REGULATIONS

The history of liquor taxation is not a pleasant one. No industry has been taxed as heavily as the legal distillers, not only in the United States, but throughout the world. On the one hand, governments have laid an unduly heavy burden on the legal producers of distilled beverage spirits. On the other hand, dishonest men have evaded legal obligations and brought the industry into disrepute. Moreover, in many instances, dry interests have attempted to further their cause of prohibition by advocating confiscatory high taxes. For example, in England, by 1730, the laws were so complicated and onerous that they all but destroyed the industry, and Parliament, realizing that the higher the taxes, the less the income, completely revised regulations in 1743. Whenever legislators forgot the law of diminishing returns, illicit distilling flourished.

Government regulations pertaining to alcoholic beverages find their beginning in one of the very earliest bodies of law, the Babylonian Code of Hammurabi, nearly 2000 years before Christ, which contained provisions for the quality, sale, and use of fermented liquors. In the Magna Carta a clause provided a standard of measurement for the sale of ale and wine. With the increase in use of distilled spirits in Europe, governments became less interested in quality and more in revenue. Parliament, in 1643, set the first tax on distilled spirits at eight pence per gallon. After the Restoration, on December 25, 1661, a tax of four pence was placed on every gallon of "Aqua Vitae" distilled. A few years later, Charles II lowered the tax to two pence a gallon. From that time to the present the tax has been increased—with many fluctuations, of course.

The first liquor tax in the United States (two guilders on each half vat of beer) was imposed in 1640 by William Kieft, Director General of New Netherland. The Molasses Act of 1733 and the Sugar Act of 1763, overtaxing the import of French and Dutch rum and molasses and leaving the more expensive British products free, provoked united protest and action against its enforcement.

In 1791, Alexander Hamilton, in testing the strength of the new Federal Government, imposed an excise tax of seven cents for each gallon produced and fifty-four cents per gallon of still capacity to be collected by revenue officers assigned to each district. Hamilton's fiercely contested federal excise tax was repealed in 1800 during Jefferson's

administration, and except for the years between 1812–1817, as a war measure, there was no further excise tax on domestic beverage spirits until 1862.

In 1960 the combined federal excise tax and the average state tax (32 states) amounted to \$12.27 per proof gallon (federal tax—\$10.50 per proof gallon). Table 1 lists the federal excise tax rates for various years.

Table 1. Federal Excise Tax Rates on Distilled Spirits

Year	Rate ^a	Year	Rate ^a
1812–1817	\$0.09	1934 (January)	2.00
1862	0.20	1938 (July)	2.25
1864 (July)	0.60	1940 (July)	3.00
1864 (December)	2.00	1941 (October)	4.00
1894	1.10	1942 (November)	6.00
World War I	2.30	1944 (April)	9.00
1919	6.40	1951 (November)	10.50
1933 (December)	1.10		

^a Per tax gallon.

In the United States, the revenue from excise taxes on distilled spirits has become a substantial part of income realized by the three levels of government; federal, state, and local. In 1863, with a \$0.20 rate, the Federal Government collected over \$5 million, while in 1960 the total revenue amounted to \$3,090 million, of which 73% represented the Federal Government’s share, amounting to \$10.50 per gallon. From Repeal through 1960, over \$48 billion have been paid into the treasuries of the three levels of government by the beverage distilling industry. This does not include the normal federal, state, and local corporate taxes of all types generally paid by industry.

Supervision over the production of distilled beverage spirits is maintained by the Alcohol and Tobacco Tax Division of the Internal Revenue Service which succeeded the Alcohol Tax Unit on March 15, 1952. This organization’s enforcement agents are charged with the responsibility of eliminating illicit operations which deprive the legal industry of extended markets and the government from realizing enormous tax revenues. Operating under a handicap of minimum enforcement personnel, which Congress is unwilling to remedy, the ATTD in 1959, with 884 investigators, seized 9,225 stills, 225,232 gallons of distilled spirits, over 4½ million gallons of mash, 3,193 vehicles and property appraised at almost \$3 million, and made 10,912 arrests. This does not include the seizures made by state and local enforcement agents.

Prior to Prohibition, revenue agents and deputy collectors investigated illegal liquor operations, made arrests, seizures, etc, along with income tax and other miscellaneous work. On January 16, 1920, the effective date of Prohibition, federal prohibition agents took over the duties. An act of Congress created the Bureau of Prohibition in the Treasury Department on April 1, 1927. The Prohibition Reorganization Act, effective July 1, 1930, terminated the Bureau of Prohibition and created the Bureau of Industrial Alcohol in the Treasury Department, responsible for the permissive provisions of the Act, and the Bureau of Prohibition in the Department of Justice, responsible for the enforcement of the penal provisions of the National Prohibition Act. These two were merged on December 6, 1933, as the Alcohol Tax Unit, Internal Revenue Department.

During Prohibition in 1928, agents seized 16,220 illicit distilleries, 18,920 stills, 9,133 still worms, 217,278 fermenters, 1,048,636 gallons of distilled spirits, 28 million gallons of malt, wine, etc, over \$13 million in property, and made 75,307 arrests. This awesome total does not include state and local seizures.

PRODUCTION AND CONSUMPTION

The production of distilled beverage spirits has generally kept pace with consumption. In 1810, according to government records, Pennsylvania produced 6½ million gallons, Indiana 22,000 gallons, and Kentucky over 2 million gallons. Apparently in anticipation of Prohibition, 300 million gallons of beverage spirits was produced in 1917, of which 60 million gallons was whisky. In the year 1930, the Prohibition Enforcement Bureau estimated that the illicit production amounted to 800 million gallons.

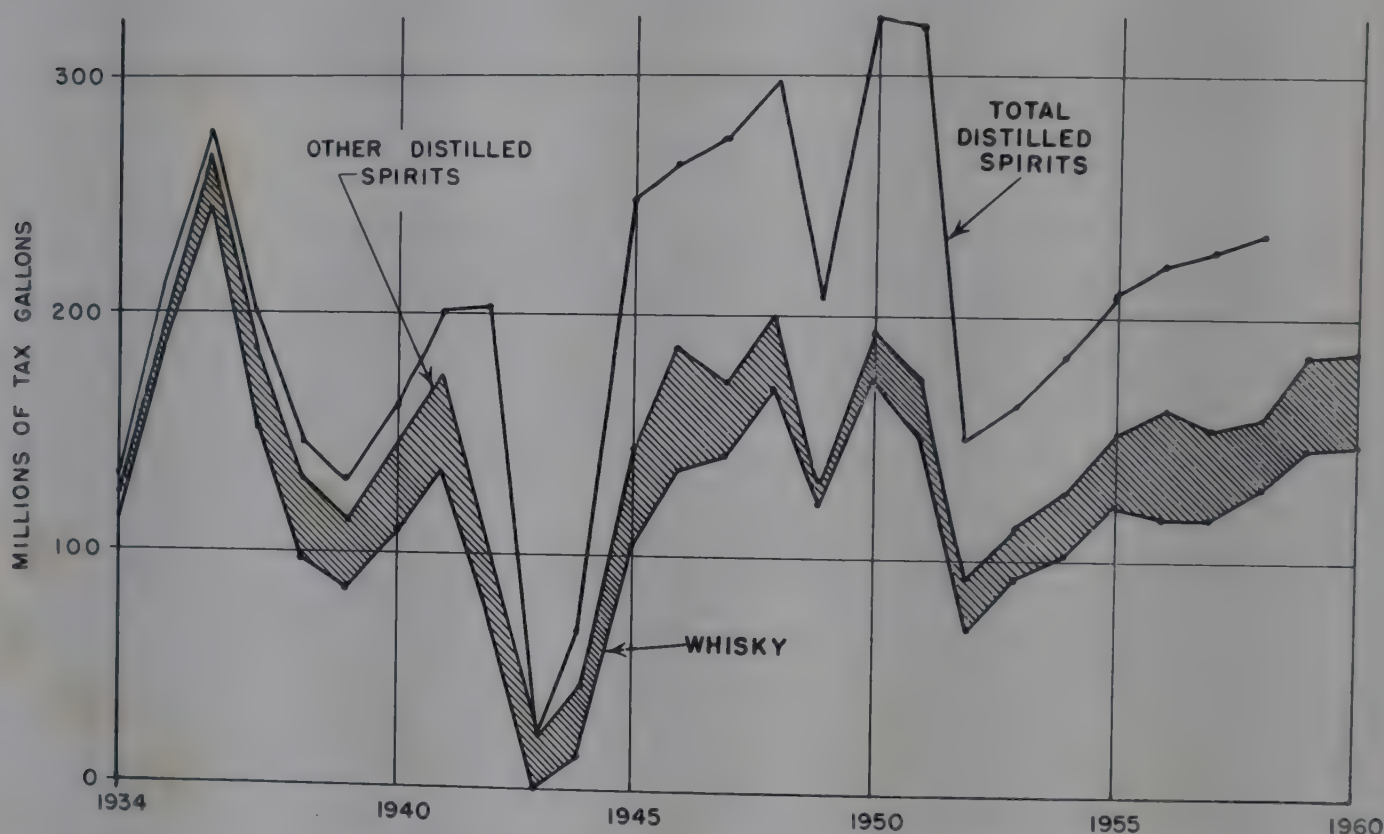


Fig. 2. Production of distilled spirits, 1934-1960.

After Repeal, the industry, literally starting again from the beginning, produced almost 108 million gallons of whisky in 1934 and reached an all-time high of 245 million gallons in 1936. Since then, with the exception of 1950 and 1951, production has mostly been on an inventory replacement basis in line with the expected increase in total consumption due to the steady increase in population. Some apprehension over the Korean police action caused a substantial increase in production in 1950 to 174 million gallons. However, only 68 million gallons were produced in 1952.

In 1960, 186,822,123 gallons of beverage spirits was produced, including 148,915,351 gallons of whisky. Figure 2 shows the production figures of distilled spirits from 1934-1960.

The maturation process is responsible for a loss of product, due to evaporation and initial soakage; approximately a 3½% loss per year is experienced.

In 1960 the consumption of beverage spirits reached 234 million wine gallons, of which 75.1% represented American, Scotch, and Canadian whiskies; seven brands out of the leading ten in sales were blends. Since 1949, whisky consumption decreased from 87.8% to 75.1% in 1960 of the total liquor consumption. At the same time, American whiskies decreased from 80.3% in 1949 to 60.8% in 1960. Most of this can be accounted for by the growing popularity of Canadian and Scotch whiskies, gin, and vodka, all of which show a substantial increase. Table 2 shows the U. S. consumption of liquor, by types, for 1949 and 1960.

Table 2. Liquor Consumption by Types (U.S.A.)^a

Type	1949 ^b	1960 ^b
blends	66.2	31.3
straights	8.7	25.4
bonds	5.4	4.1
Scotch	4.4	8.1
Canadian	2.7	5.2
other	0.4	0.3
total whisky	87.8	74.4
gin	7.1	9.3
vodka	0.0	7.8
cordials	2.2	3.8
brandy	1.3	2.6
rum	1.3	1.6
other	0.3	0.5
total non-whisky	12.2	25.6
total consumption, million wine gallons	169.5	234.7

^a According to *Business Week*, Feb. 17, 1962.

^b Percent of total liquor consumption.

Standards of Identity

Unlike most substances in this universe which can be identified scientifically (generally according to chemical structure or composition) and then named accordingly, distilled alcoholic beverages are characterized by their geographical origin, type of material used in production, and standard of quality, as evaluated by organoleptic analysis (taste and bouquet).

Since secretiveness was a way of life for most ancient distillers, this philosophy has come to prevail and each individual producer today operates according to his own methods in the way he feels will be best for his own product. Moreover, since chemical analyses in this area are not fine enough, it is not possible to correlate taste and bouquet with chemical composition. Evaluation then becomes a matter of taste and odor techniques (organoleptic analysis).

Over the centuries, legends, traditions, and to some extent political influences were great factors in the production and identification of potable distilled liquors. Since most governments were involved economically because of the great source of revenue realized, it was not too surprising to have these same governments establish standards for distilled alcoholic beverages, generally in keeping with the historic customs prevailing in their country. As a result, geographical identification has become accepted, and each country respects the identity and exclusiveness of the other's products.

Within each category of product there can be wide variations in the flavor which can be caused by (1) types of materials and their proportions, (2) methods of material preparation, (3) selection of yeast types, (4) fermenter conditions, (5) distillation processes, (6) maturation techniques, and (7) blending experience.

Since the alcoholic and water components are relatively insignificant factors in flavor intensity or palatability, distillers are primarily interested in the more flavorful constituents—the so-called “congeners” (substances that are generated with the alcohol during the fermentation process and, also, in the course of maturation). It follows, therefore, that in order to produce a palatable product, it is necessary to select the proper configuration of these constituents (congeners). In consideration of items 1–7 above, it is quite impossible to accomplish this by production techniques alone, and for that reason the majority of alcoholic beverages offered in world markets are blended to provide uniformity, balanced bouquet, and palatability. To illustrate the variations in flavor constituents an analysis of the leading brand in each category is given in Table 3.

Table 3. Congeneric Content of Major Types of Distilled Alcoholic Beverages^a

Component ^b	American blended whisky	Canadian blended whisky	Scotch blended whisky	Straight bourbon whisky	Bonded bourbon whisky	Cognac brandy
fusel oil	83	58	143	203	195	193
total acids (as acetic acid)	30	20	15	69	63	36
esters (as ethyl acetate)	17	14	17	56	43	41
aldehydes (as acetaldehyde)	2.7	2.9	4.5	6.8	5.4	7.6
furfural	0.33	0.11	0.11	0.45	0.90	0.67
total solids	112	97	127	180	159	698
tannins	21	18	8	52	48	25
total congeners, wt/vol %	0.116	0.085	0.160	0.292	0.309	0.239

^a The above determinations were made according to the official methods of analysis of the Association of Official Agricultural Chemists. Fusel oil was determined by the Komarowsky colorimetric method. Foster D. Snell, Inc.

^b Grams per 100 liters at 100° proof.

WHISKIES

Although brandy, rum, and gin are substantial items in world markets, whiskies are by far the leading distilled alcoholic beverages, with those from Canada, Scotland, and the United States accounting for most of the sales. Irish whiskey, a distinctive product of Ireland, while not enjoying a large volume of sales, does have good distribution and remains a specialty item among the world's whiskies. The Irish use the spelling “whiskey,” the Scotch and Canadians “whisky,” and the Americans use both, although U.S. regulations use the spelling “whisky.”

Canadian. Canadian whisky is a distinctive product of Canada, manufactured in Canada in compliance with the laws of Canada regulating the manufacture of whisky for consumption in Canada and containing no distilled spirits less than two years old. Actually Canadian whiskies are premium products usually bottled at six

years of age or more, and since they are blended, they are not designated as straight whiskies. They are light-bodied and, though delicate in flavor, they nevertheless retain a distinct positive character. The Canadian government exercises the customary rigid controls in matters pertaining to labeling of products and in collection of the excise tax. However, it sets no limitations as to grain formulas, distilling proofs, or special types of cooperage for the maturation of whisky. Its policy is to rely on its distillers to be the judges of what their home and world markets require, and the record in terms of worldwide consumer acceptance attests to the wisdom of this policy.

The major cereal grains, corn, rye, and barley malt, are used in the production of Canadian whiskies. The proportions of each grain in the mashing formula remains a distiller's trade secret; otherwise, the process is substantially the same as is found in the major distilleries of the United States. Since Canadian distillers are not faced with artificial proof restrictions in their distillation procedures, they are able to operate batch and continuous distillation systems under conditions that are optimum for the separation and selection of desirable congeners. With such techniques it is possible to take advantage of the physical relationships that exist between the beverage spirits and the congeners that are in solution in the fermented mash.

White oak casks (50 U.S. gallons) are used in the maturation process. A substantial amount of Canadian whiskies are stored in matured cooperage which offers a unique compatibility for the whiskies produced for delicacy of flavor. Again, the proportions of new and matured cooperage used for maturation is each distiller's trade secret.

Scotch. Scotch whisky is a distinctive product of Scotland, manufactured in Scotland in compliance with the laws of Great Britain regulating the manufacturing of Scotch whisky for consumption in Great Britain and containing no distilled spirits less than three years old. This minimum age requirement is greatly exceeded by the Scotch distillers. For example, nothing under four years of age is included in their exports to the United States, and for the most part, six, eight, ten, and twelve year minimum ages are featured in their brands. Most Scotch brands are blends of grain whiskies and numerous distinctive malt whiskies produced by over 100 distilleries in four major areas of Scotland. The Highlands are noted for their clear, soft, and light-bodied whiskies. The Lowlands produce a desirable type which is sometimes called "silent" because of its lightness. In Islay off the southwest coast and in the Campbeltown area in the Firth of Clyde are the other two types of malts—high in flavor intensity and robust in character.

As in Canada, there are no government limitations placed on production and maturation techniques. The Scotch distillers are guided by their production experience developed over many centuries and by the consumer reaction to their products.

The outstanding taste characteristic of Scotch, its subtle "smokey" flavor, is due to the techniques used in the production of malt whiskies. Malted barley, dried over peat fires, is the only grain ingredient in the mash. The kind and the amount of peat used in the fires determines the intensity of flavor in the final product. Peat is substantially heather, fern, and evergreen that have been subjected to nature's ageing and compression processes over the centuries.

The dried malted barley is ground to a grist, gelatinized in a mash tub, and after conversion is completed, the liquid portion or "wort" is drained off, cooled, and placed in a fermenter.

After fermentation is complete, the separation of malt whisky from the fermented

wort takes place in a batch distillation system—a copper kettle with a “worm” or spiral tube leading from its head. The size and shape of these pot stills exert a definite influence on the character of the whiskies. Another critical factor is the selection of the product during that portion of the distillation cycle which will produce the desired flavors. The first portion in the cycle is referred to as “fore shots” and the last as “feints” (heads and tails in the United States). The middle portion, after further distillation, becomes “high wines,” and is subsequently reduced to maturation proof for storage in oak casks. The final distillation proof is in the 122–142° range.

The grain whiskies used in Scotch brands are produced in a manner similar to the production techniques used in Canada and in the United States. Corn (referred to in the United Kingdom as “maize”), rye, and barley malt are the ingredients. The proportions again depend on the individual distiller. Since delicate flavors are desired, the distillation proof is around 180–186°. The distillation system is, basically, a Coffey still, composed of two columns.

The grain whiskies are generally aged in matured oak casks not unlike American and Canadian barrels. Some malt whiskies acquire other distinctive qualities by being matured in oak casks which were previously used for sherry. Whereas the materials, geographic location, and the production processes are responsible for the uniqueness of Scotch whisky, it is the skill of the blender that makes possible the final achievement—a uniform, pleasant product with a unique taste and aroma. As many as twenty, and sometimes more, different malt and grain whiskies are harmoniously “married” to produce a brand. Of course, the formula is a well-guarded secret.

Irish. Irish whiskey is a distinctive product of Ireland, manufactured either in the Irish Free State or in Northern Ireland, in compliance with their laws regulating the manufacture of Irish whiskey for home consumption, and containing no distilled spirits less than three years old. Like Scotch, Irish whiskies are premium blends of grain and malt whiskies. Unlike Scotch, Irish whiskey does not have the unique smokey taste because the barley malt is not dried over peat fires. Since whiskey has been known in Ireland as long as in Scotland, it is not surprising that the production techniques are very closely related to those used in Scotland. One variation, however, is the use of some small grain in addition to barley malt in the production of malt whiskey. Irish whiskey brands are generally considered to be more flavorful and heavier-bodied than Scotch whiskies.

American. Distilled spirits for beverage purposes in the United States are characterized specifically as to type, materials, composition, distillation proofs, maturation proofs, storage containers, and the extent of the ageing period. The Federal Government also requires that a detailed statement of the production process be filed for each type, and any subsequent improvements or changes must be filed and approved before being placed into operation. In addition, a generalized application of the regulations is made to establish the identity of products where the intensity of flavor may not conform to an arbitrary organoleptic evaluation based on a chemical analysis of the product. As a result, in spite of extensive manufacturing facilities and know-how available for the production of a wide range of whiskies for the improvement of palatability, the distiller is restrained within narrow limits and does not enjoy the wide degree of latitude available to the Canadian and Scotch distillers.

American regulations, although specific in detail, reflect a wide divergence of opinion that has prevailed in past years in some geographical areas of the United States as to what product represents the consumer's choice.

Title 27, Code of Federal Regulations, Subpart C, lists ten types of whisky which "shall be deemed 'American type' whiskies." Only the types which are major factors in the American market will be identified, other than a general description of whisky and grain neutral spirits.

Whisky. An alcoholic distillate from a fermented mash of grain distilled at less than 190° proof in such a manner that the distillate possesses the taste, aroma, and characteristics generally attributed to whisky. Any cereal grain qualifies as the raw material. Since this product does not qualify as a straight whisky, it has very little application, and consequently almost none is produced.

Grain Neutral Spirits. An alcoholic distillate from a fermented mash of grain distilled at or above 190° proof. There is no type of cereal grain requirement. However, corn is generally the preferred grain. Varying only in the proof of distillation and intensity of flavor, grain neutral spirits require the same mashing and fermentation processes as whisky and may be stored in new or matured cooperage.

During storage, grain neutral spirits acquire a degree of maturation similar in nature to the grain whiskies of Great Britain and to some of the delicate whiskies of Canada. In effect, grain neutral spirits are highly refined whiskies. United States labeling regulations will not permit the use of an age statement for grain neutral spirits, and consequently most of the consuming public is unaware that this refinement is included in the products they purchase. The most popular brands in the blend category use varying proportions of matured grain neutral spirits in their formulas.

Whisky—Rye, Bourbon. "Rye whisky," "bourbon whisky," "wheat whisky," "malt whisky," or "rye malt whisky" is whisky which has been distilled at not exceeding 160° proof from a fermented mash of not less than 51% rye grain, corn grain, wheat grain, malted barley grain, or malted rye grain, respectively, and stored in charred new oak containers. They also include mixtures of such whiskies where the mixture consists exclusively of whiskies of the same type. Corn whisky has the same distillation proof limitation (160°). However, it must be produced from a fermented mash of not less than 80% corn grain and stored in uncharred oak containers or reused charred oak containers.

In producing bourbon whisky, for example, the mashing formula must contain at least 51% corn and the remaining ingredients (49%) generally are proportioned between rye grains and barley malt. Each distiller selects the formula that he feels will produce his type bourbon. Very little bourbon with 49% small grains is produced. The most popular proportions are 60% corn, 28% rye, 12% barley malt (referred to as 40% small grains), 70–18–12 (30% small grains), and 75–13–12 (25% small grains). While some bourbons use as much as 15% barley malt, the general practice in the industry is to use 12% barley malt for all bourbon production.

Since rye and barley malt produce more intensive flavors than corn, the formula with the greater small-grains proportion will produce a bourbon with more body, provided, of course, that the same distillation techniques are used.

Straight Whisky. Any of the whisky types mentioned above further qualify as "straight whisky" by complying with the following: (1) withdrawn from the distillery at not more than 125° and not less than 80° proof (for maturation purposes); (2) aged for not less than 24 calendar months.

The regulations permit the mixing of straight whiskies provided they are homogeneous and, further, provided that the age of this mixture be identified with the age of the youngest whisky in the mixture. Most straight whiskies on the market greatly

exceed the minimum age requirement because each distiller attempts to age his product until he feels his whisky has reached the ripeness or maturity which is ideal for that particular whisky. Most authorities agree that the average bourbon attains this organoleptic stage in about six years.

A straight whisky may further be identified as *bottled in bond* provided it is at least four years of age, bottled at 100° proof, and distilled at one plant by the same proprietor. A bottled-in-bond whisky may contain homogeneous mixtures of whiskies, provided they represent one season, or if consolidated with other seasons, the mixture "... shall be the distilling season of the youngest spirits contained therein, and shall consist of not less than 10% of spirits of each such season." January through June is designated as Spring, and July through December is designated as the Fall season. The federal regulations allow the federal excise tax payment to be delayed until after bottling and removal from bonded case storage. All other American-type whiskies must pay the tax upon withdrawal of the whisky from maturation storage in bonded warehouses.

Blended Whisky (Whisky—A Blend). Blended whisky is a mixture which contains at least 20% by volume of 100° proof straight whisky and, separately or in combination, whisky or grain neutral spirits. In addition, like all American-type whiskies, the bottling proof must be at least 80° proof. When a blended whisky contains at least 51% by volume of straight whisky (bourbon, for example) it may be identified as blended bourbon whisky or bourbon whisky—a blend.

Just as the minimum age requirements are exceeded by distillers on their straight whisky brands, those distillers that market popular brands of blends greatly exceed the minimum requirements set forth by the regulations. As a result, as many as 40 whiskies and matured grain neutral spirits may be utilized harmoniously to achieve a blended whisky. As with the Canadian and Scotch distillers, the final achievement in producing a well-balanced blend, of exceedingly consistent uniformity, with a high degree of organoleptic attainment depends on the experience and skill of the blender. Of course, with the wide spectrum of whisky flavors available, as represented by the many types of bourbons and matured grain neutral spirits plus some ryes, the blender has a greater opportunity to enhance the palatability of his product. In the United States, brands with a proportion of 35% straight whiskies to 65% grain neutral spirits comprise a majority of the sales in this category.

GIN

Francis de La Boe, a 17th century professor of medicine at Leyden University, Holland, is credited with being the originator of the botanical, flavored beverage spirits known as gin. Since his product's primary flavor was due to the essential oils extracted from juniper berries, he gave it the French name "jénîèvre," which appeared later as the Dutch "geneva" and finally was abridged to the English "gin." *Distilled gin* is a distillate obtained by original distillation from mash, or by the redistillation of distilled spirits, over or with juniper berries and other aromatics customarily used in the production of gin. Gin derives its main characteristic flavor from juniper berries. In addition to juniper berries, other botanicals may be used, including angelica root, anise, coriander, caraway seeds, lime, lemon and orange peel, licorice, calamus, cardamon, cassia bark, orris root, and bitter almonds. The use and proportion of any of these botanicals in the gin formula is left to the producer, and the character and quality of the gin will depend to a great extent on the skill of the craftsman in

formulating his recipe. The more discerning producers formulate their aromatic ingredients on the basis of the essential oil content in the raw materials to assure a greater degree of product uniformity.

To expose the essential oils, the ingredients are reduced to a granular form and then immersed directly into the kettle (pot) which is filled with grain neutral spirits at approximately 100° proof. A vapor phase extraction may also be used. In this case the botanical mixture is placed on trays or in baskets in the head of the kettle where the alcoholic vapors, in passing through, extract the essential oils and rise to the condenser.

It is important that the grain spirits be as neutral as possible (devoid of congeners) to ensure that no undesirable flavors be imparted to the gin. In addition to the kettle, some gin stills have a refinement section (as many as six plates) above the kettle for flavor stability and enrichment. Indirect steam heat is applied and the various essential oils are distilled over during the entire distillation cycle. The first portion (heads) and the last portion of the cycle (tails) are not included in the product. Only the heart of the run is used and it represents approximately an 85% recovery of the original alcohol concentration in the kettle. This, of course, varies with the type of product that is desired by the producer. Some distillers, to avoid thermal decomposition of the delicate flavors and to acquire a degree of softness, conduct distillation under reduced pressure at a temperature of about 135°F. *London Dry Gin* is produced in accordance with the procedures described in this paragraph.

In Great Britain and Canada the regulations permit and recognize the use of maturation techniques for gin. Gins stored in special oak casks acquire a pale golden hue and a unique "dryness" of flavor. Although distillers are permitted to mature gins in the United States for further flavor development, the Federal Government does not permit an age claim or any reference to ageing to appear on the label.

Holland Gin, characterized by its high flavor intensity derived mostly from juniper berries and cereal grains (corn, rye, barley malt), is produced by immersing the botanical mixture directly into the grain mash prior to distillation or by extracting the essential oils from the botanical mixture with the heavy distillate (high wines) from a fermented mash of grain, consisting of corn, rye, and barley malt. As a consequence, the flavors produced during fermentation become flavor components of the final product.

Compound gin is a mixture of grain spirits and proportions of essential oil extracts from botanicals. It does not undergo any distillation procedure. It is practically nonexistent in the market.

BRANDY

"Brandy" is a distillate or a mixture of distillates obtained solely from the fermented juice, mash, or wine of fruit, or from the residue thereof, distilled at less than 190° proof in such manner as to possess the taste, aroma, and characteristics generally attributed to the product. The most important category of brandy is "fruit brandy," distilled solely from the juice or mash of whole, sound, ripe fruit or from standard grape, citrus, or other fruit wine. When brandy is derived exclusively from one variety of fruit, it is designated by the name of such fruit. However, a fruit brandy derived exclusively from grapes may be designated as "brandy" without further qualification. Unless the product is specifically identified, the term brandy always means grape brandy and is, therefore, a distillate obtained from grape wine. Brandy is subject to a distillation limitation of 170° proof. If distilled over 170° proof, it must be further identified as "neutral brandy." A minimum of two years' maturation in oak casks is

required or otherwise the term "immature" must be included in the designation of the brandy. While the age is not carried on the label, brandies are normally aged from three to eight years.

Brandies are produced in batch or continuous distillation systems. The pot still or its variation is universally utilized in France. In the United States brandies are produced in both systems. The batch system produces a more flavorful product; the continuous system produces a lighter, more delicate flavor.

The history of brandy can be said to be the history of distillation, because in the dim past it was the distillation of wine in crude stills that gave "Aqua Vitae" to the world. In the ensuing evolution, many geographical areas of Europe and of the United States became renowned for their brandies. Perhaps the best known and most popular brandy in the world comes from the Cognac region of France, the Department of Charente and Charente Inférieure. As such, it enjoys an exclusive identity, *Cognac*, under which no other brandy may be labeled. Cognac is produced on the traditional pot stills by small farmer-distillers for sale to the bottlers who age the brandies in limousin oak casks, made of oak from the forests of Limoges. When the brandies reach maturity, they are skilfully blended for marketing under their own brand name.

Cognac is a blend of some Grande Champagne, Petite Champagne, Borderies, and Fins Bois—the proportions of each a well-kept secret and in accordance with the desire of each individual distiller to produce a quality product. To further characterize Cognac, the bottle labels carry letters having the following meanings: *E*, Especial; *F*, Fine; *V*, Very; *O*, Old; *S*, Superior; *P*, Pale; *X*, Extra; *C*, Cognac. For example, *VSOP* means Very Superior Old Pale, and is therefore considered to be a particular shipper's better quality product.

Another well-known brandy of France is *Armagnac* which is produced near Conçon, in the Department of Gers in southern France. Armagnac is distilled from wines made from the Piquepoul, the Colombard, Jurançon, and Meslier grape varieties on a continuous system using two pot stills in series. The black oaks of Gascony provide the wood for the casks which are used for ageing Armagnac. It is not uncommon to find Armagnac bottled as a vintage brandy, ie, the distillation from one year. Armagnac is considered to be more heavy-bodied and drier than Cognac.

There are brandies distilled in almost every wine region of France; they are called *eau de vie*, and when exported are simply referred to as French Brandy, never as Cognac.

In the United States, California produces almost all of the grape brandy. Generally, it is a well integrated operation—the cultivation of the grapes, the making of the wine, the distilling, ageing, bottling, and the marketing of the brandy being done by the same firm. Distillation is usually accomplished on a continuous, multicolumn distillation system. Of the total brandy consumption in the United States (approximately 6.5 million gallons), California brandies account for over 65%.

Other geographic areas in Europe and in South America are well known for their specialty brandies. Among these are earthy flavored Spanish brandies, distilled from Jerez sherry wine; the fragrant, fruity Portuguese brandies, distilled from port wine; the pleasant and flowery muscat bouquet of Pisco brandy from Peru; kirschwasser brandy, with its almond undertone flavor, distilled from a fermented mash of small black cherries which grow along the Rhine Valley in Germany and Switzerland; and slivovitz, the plum brandy which is produced in Hungary and in the Balkan countries.

RUM

"Rum" is any alcoholic distillate or mixture of distillates from the fermented juice of sugarcane, sugarcane syrup, sugarcane molasses, or other sugarcane by-products, distilled at less than 190° proof in such a manner that the distillate possesses the taste, aroma, and characteristics generally attributed to rum. "New England Rum," produced only in the United States, is distilled at less than 160° proof and is marketed as "straight rum," ie, it is not blended. The fairly low distillation proof and the traditional production methods in vogue for over 300 years make New England Rum characteristically heavy in body and high in flavor intensity.

Blackstrap molasses, a by-product of sugar production, is by far the most common raw material used in the manufacture of rum. Otherwise, the same basic factors which produce different whiskies are responsible for the varieties of flavors of rums. The type of yeast, fermentation environment, distillation techniques and systems, the maturation conditions, and not least the blending skill are important in determining the final character and quality of rum.

Rums are characterized as light-bodied, of which the rums of Puerto Rico and Cuba are the best known, and as full-bodied, rums which come from Jamaica and certain other islands of the West Indies. Light rums are distilled on multicolumn continuous distillation systems over a proof range of 160 to 180°. They are matured in oak casks which are reused for rum storage.

Jamaica and other full-bodied rums are distilled between 140 and 160° proof in pot stills. They are matured in large casks (111.6 gallons) called "puncheons." Unlike the light-bodied rums which use cultured yeast for inoculation, the Jamaica rum relies on natural fermentation, sometimes referred to as "wild" fermentation. In this method the mash is inoculated by the yeast that is present in the air and in the raw material.

Puerto Rican rums are generally labeled either as white or as gold label. The latter is a little more amber in color and has a more pronounced flavor intensity. Although the rums produced in various geographic areas are not considered distinctive types, they do retain their geographic significance and such names may not be applied to rum produced in any other place than the particular region indicated in the name.

CORDIALS AND LIQUEURS

Cordials and *liqueurs* are synonymous terms, with the former ascribed to American origin and the latter of European extraction. They are products obtained by mixing or redistilling neutral spirits, brandy, gin, or other distilled spirits with or over fruits, flowers, plants, or pure juices therefrom, or other natural flavoring materials, or with extracts derived from infusions, percolations, or maceration of such materials. Cordials must contain a minimum of 2½% by weight of the finished product, sugar or dextrose, or a combination of both. However, if the added sugar and dextrose are less than 10% by weight of the cordial, then its designation may include the term "dry." Synthetic or imitation flavoring materials cannot be included in United States cordials, nor can they be designated as "distilled" or "compound."

Cordials were known to be in existence during the days of the Pharaohs and the ancient Athenians, but commercial production of cordials dates back to the Middle Ages when the alchemists, physicians, and the mystical monks were all searching for an elixir of life. From all this activity there were developed many well-known cordials,

such as Benedictine and Chartreuse, both aromatic plant flavor derivatives and both bearing the names of the fraternal orders by whom they were prepared.

The variety of cordials is very great, simply because of the wide spectrum of flavors that are available from the fruits, peels, leaves, roots, herbs, and seeds flourishing on this earth. Organoleptic attainment, however, becomes a matter of experience and skill in the selection of botanicals and in the extraction and formulation of flavors. Although these elements are carefully guarded secrets, the producer must rely on three well-known basic methods of production; viz, maceration, percolation, and distillation, or any combination thereof.

Maceration involves the steeping of the raw materials in the beverage spirits, usually in a vat, until the beverage spirits have acquired the desired aroma, flavor, and color. The liquid is then drawn off and provides the base for further processing.

Percolation is accomplished by recirculating the beverage spirits through a percolator which contains the raw materials. As the beverage spirit seeps down through the raw material, it extracts and removes the desired constituents which will give the proper aroma, flavor intensity, and color.

The *distillation* method is similar to that used in gin production. The ingredients are either immersed in the beverage spirits or placed in trays or pans in the head of the still. The rising vapors extract the essential flavors, which are then condensed and discharged as a colorless liquid. This distillate contains the basic flavor which is used for further processing.

Cordials are characterized and marketed according to their generic names; for example, Anisette (aniseed), Creme de Menthe (peppermint), Triple Sec (citrus fruit peel), Sloe Gin (sloe berries), and by their trade names (proprietary brands) of which Benedictine and Chartreuse are well known examples.

VODKA

Over the past ten years, the drinking pattern of the United States consumer has become more widely diversified. Vodka, United States variety, has moved up in sales from practically nothing in 1949 to 8% of the beverage spirits sales in 1961. The fact that it can be mixed with any flavorful substance that might appeal to the consumer seems to be the motivating factor for its wide acceptance. Vodka, produced on a multicolumn distillation system from a fermented mash of grain at or above 190° proof, must be further treated with charcoal or activated carbon or further refined by distillation in such a manner as to be without character, aroma, or taste. If any flavoring material is added to the distillate, the vodka is characterized with the name of the flavoring material used.

The Manufacturing Process

Any material rich in carbohydrates is a potential source of ethyl alcohol, which for industrial purposes is obtained by the fermentation of materials containing sugar (molasses), or a substance convertible into sugar, such as the starch in grains, and also from other sources (see Ethanol) such as petrochemical processes. In the production of distilled spirits for beverage purposes, however, cereal grains are the principal types of raw material used. Any reference to "alcohol" in beverages is always to ethyl alcohol, C_2H_5OH . Although other alcohols may be present, they are referred to as "higher alcohols," "fusel oils," or are termed specifically as amyl, isoamyl, etc.

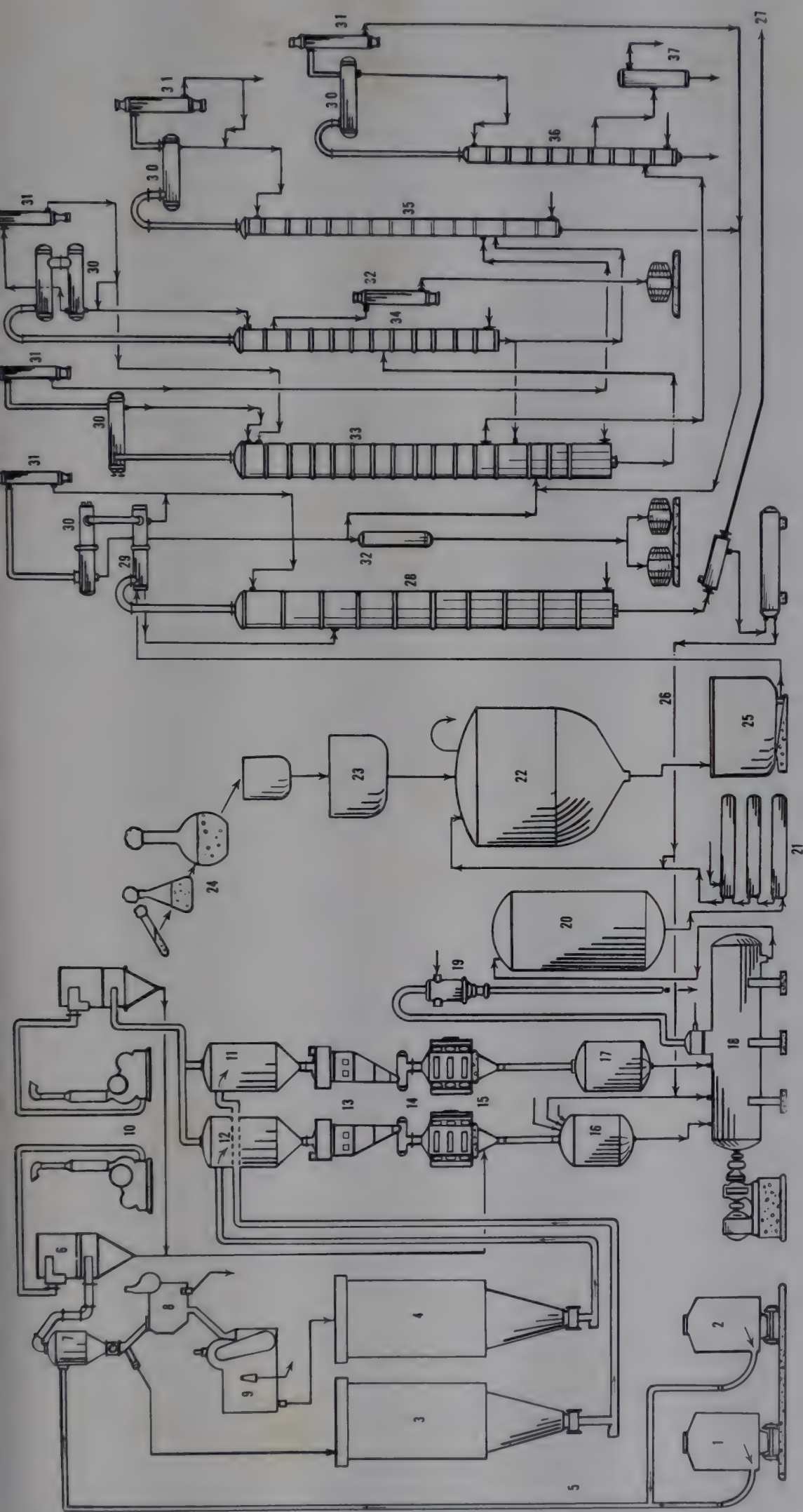


Fig. 3. Material process flow, modern beverage spirits plant.

- | | | |
|-----------------------|---|------------------------------------|
| 1. Cereal grains | 20. Converter | 29. Heat exchanger |
| 2. Malt | 21. Mash coolers | 30. Dephlegmator |
| 3. Malt bin | 22. Fermenter | 31. Vent condenser |
| 4. Cereal grain bin | 23. Final yeast propagator | 32. Product cooler |
| 5. Unloading elevator | 24. Yeast culture and intermediate yeast propagator | 33. Selective distillation column |
| 6. Dust filter | 25. Fermented-mash holding vessel | 34. Product concentrating column |
| 7. Collector | 26. Stillage return system | 35. Aldehyde concentrating column |
| 8. Scalperator | 27. Stillage flow to recovery system | 36. Fusel oil concentrating column |
| 9. Millerator | 28. Whisky separating column | 37. Fusel oil decanter |

The chemical composition of grain varies considerably and depends to a large extent on environmental factors, such as climatic conditions and the nature of the soil upon which it is grown. Another variable is introduced in the use of malt (sprouted or germinated grain). Malt is generally understood to be germinated barley, unless it is further qualified as rye malt, wheat malt, etc. The purpose of malting is the development of the amylases, the active ingredients in malt. Amylases are enzymes of organic origin, and change grain starch into the sugar, maltose. Besides providing the means of converting the grain starch into sugar, the malt is also a contributing factor to the final flavor and aroma of the distillate. The malting techniques may produce a malt of such unusual character that it may indeed furnish the outstanding characteristics of the final product, as in Scotch whisky. For more about the process of malting see *Malts and malting*.

Figure 3 shows the material process flow for a modern beverage spirits plant.

DEFINITIONS

Bushel. A "distillers bushel" of any cereal grain is 56 pounds.

Proof. In Canada, Great Britain, and the United States, the alcoholic concentration of beverage spirits is expressed in terms of "proof." The U.S. statutes define this standard as follows: "Proof spirit shall be held to be that alcoholic liquor which contains one-half its volume of alcohol of a specific gravity of 0.7939 at 60°F." More simply, the figure for proof is always twice the alcoholic content by volume. For example, 100° proof means 50% alcohol by volume. In Great Britain as well as Canada, "proof spirit is such as at 51°F weighs exactly twelve-thirteenths of the weight of an equal bulk of distilled water." A proof of 87.7° would indicate an alcohol concentration of 50%. A conversion factor of 1.14 can be used to change British proof to U.S. proof (see *Ethanol*).

Proof gallon. "A U.S. gallon of proof spirits or the alcoholic equivalent thereof"; ie, a U.S. gallon of 231 cubic inches containing 50% of ethyl alcohol by volume. Thus, a gallon of liquor at 120° proof is 1.2 proof gallons; a gallon at 86° proof is 0.86 proof gallons.

A British and Canadian proof gallon is an imperial gallon of 277.4 cubic inches at 100° proof (57.1% of ethyl alcohol by volume). An imperial gallon is equivalent to 1.2 U.S. gallons. To convert British proof gallons to U.S. proof gallons, multiply by the factor 1.37. Since excise taxes are paid on the basis of proof gallons, this term is synonymous with *tax gallons*.

Congeners. The flavor constituents in beverage spirits which are responsible for its flavor and aroma and which result from the fermentation, distillation, and maturation processes.

Balling. A measure of the sugar concentration in a grain mash, expressed in degrees and approximating percent by weight of the sugar in solution.

Fusel Oil. An inclusive term for heavier, pungent-tasting alcohols produced during fermentation. Fusel oil is composed of approximately 80% amyl alcohols, 15% butyl alcohols, and 5% other alcohols.

Heads. A distillate containing a high percentage of low-boiling components such as aldehydes.

High Wines. An all-inclusive term for beverage spirit distillates which have undergone complete distillation.

Low Wines. Products of simple distillation units requiring further refinement.

Tails. A residual alcoholic distillate.

Wine Gallon. Measure of actual volume; U.S. gallon contains 231 cubic inches; British (Imperial) gallon contains 277.4 cubic inches.

GRAIN HANDLING AND MILLING

The beverage distilling industry utilizes premium cereal grains. Each distiller supplements government grain standards with his own specifications, especially in the elimination of grain with objectionable odors, which may have developed during storage or kiln drying at the elevators. Hybrid corn, usually of the dent variety, because it is readily available, and plump rye, developed from Polish strains (Rosen), are used for beverage alcohol production. The modern distilleries use airveyor unloading systems. Others use the traditional power shovel in conjunction with screw conveyors and bucket elevators. Even though the grain has been subjected to a cleaning process at the elevator, it is passed over receiving separators, a series of vibrating screens which sift out the foreign materials. Air jets and dust collectors remove any light material and magnetic separators remove metallic substances.

Milling the grain breaks the outer cellulose protective wall around the kernel and exposes more starch surface to the action of the cooking and conversion process. Distillers require an even, coarse meal without flour; for example, in corn meal the proportion may be approximately 4% on #12 screen, 12% on #16, 36% on #20, and 48% through #20; for rye meal, approximately 40% on #20, and 60% through #20; for barley malt meal, 20% on #20 and 80% through #20. The percentage of flour is ascertained by passing the meal through a #60 screen.

There are three methods of accomplishing the milling process: (1) In roller mills, using pairs of corrugated rolls (breaks) run "sharp to sharp" (projections facing projections) at differential speeds of $2\frac{1}{2}$ to 1 with approximately $3\frac{1}{2}$ bushels per inch of roll length at a fast roll speed of 500 rpm for a 9-inch diameter roll. (2) In hammer mills, where a series of revolving hammers within a close-fitting casing and rotating at 1800–3600 rpm shear the grain to a meal. The meal is removed by suction through a screen, with perforations $\frac{3}{16}$ to $\frac{5}{16}$ inches in diameter, in the bottom half of the casing. Screens are changed for each type of grain. (3) In attrition mills, which are not widely used, where the grain is ground by two counter rotating discs (1200–2000 rpm). This mill is not entirely satisfactory, because of the excessive flour it produces in the meal.

A three-break roller mill (three pairs of corrugated rolls, arranged vertically) with rolls 9 inches in diameter \times 30 inches long has a capacity of 100 bushels of corn per hour; a hammer mill 24 inches in width, 300 bushels per hour; and an attrition mill with 16-inch grinding plates, 100 bushels per hour, on the basis that 25% of the ground corn remains above the #12 mesh screens.

MASHING

Mashing is a mechanically simple process, involving *cooking*, gelatinization of starch, and *conversion* (saccharification), changing starch to grain sugar (maltose). The chemical and biological changes taking place are complex (see Enzymes) and for best results must be performed at optimum conditions of time and temperature. Cooking can be carried on atmospherically or under pressure in a batch or a continuous system.

For whisky production, batch atmospheric cooking is more widely used although some batch pressure cooking is practiced. For grain neutral spirits production, both batch and continuous pressure systems are used (see Ethanol). After cooling, conversion is accomplished in the cooking vessel by the addition of barley malt meal to the cooked grain. Some distillers pump the mash immediately to a converter for the necessary holding time and thus make the cooking vessel available for the next cook. The converted mash is cooled and pumped to the fermenters.

Each individual distiller varies his mashing procedures to suit himself, but generally all of them conform to basic principles, especially in the maintenance of sanitary conditions in the plant, in order to avoid bacterial contamination. The cooking and conversion equipment is provided with direct or indirect steam, propeller or rake-type agitation, and cooling coils or a barometric condenser. Mashing procedures for rye, corn, and malt grains are described below.

Rye. In the preparation of a bourbon mash, rye may be cooked with the corn and in that case, it generally is subjected to the corn-cooking process. However, rye undergoes liquefaction at a much lower temperature than corn, and according to some, this avoids thermal decomposition of critical grain constituents which will adversely affect the final flavor of the distillate. For that reason, many distillers mash rye separately.

Water at 100°F is drawn at the rate of 28 gallons per bushel, and rye and malt meal are added. The mash is slowly heated to 130°F and held for approximately 30 minutes. Proteolytic enzymes, active at 110–115°F, aid in reducing the viscosity, and the optimum temperature for beta amylase is 130°F. The mash is then heated to 145–152°F and held for 30–45 minutes to ensure maximum conversion. The mash (pH, 6.0) is then cooled to the fermenting temperature (68–72°F). This process of simultaneously cooking and converting small grains is called *infusion mashing*.

Corn. Although the starch in corn grains converts rather easily, higher cooking temperatures are necessary to make the starch available. Usually malt is not added at the beginning, but to reduce viscosity, “pre-malt” of one-half percent may be added before cooking, preferably at around 150°F. The addition of thin stillage (the residual dealcoholized fermented mash from the whisky distillation process) to adjust pH to 5.2–5.4 is practiced by some. For cookers operating at atmospheric pressure, a mashing ratio of 25–30 gallons of slurry (grain, water, and stillage mixture) per bushel and a holding time of 30 minutes at 212°F is preferable. The mash is cooled to 152°F and malt is added. Primary conversion, the saccharification taking place during conversion, is in the order of 70–80% of the available starches. The remainder of the conversion to fermentable sugar takes place during the fermentation process and is referred to as secondary conversion. For batch cooking under pressure, only 17–22 gallons of water are drawn, and the maximum temperature is 250–305°F. In continuous pressure cooking, water is drawn at a ratio of 24 gallons per bushel of meal and sufficient thin stillage is added to give a pH of 5.2–5.4. The mash is pumped through the continuous pressure cooker, where it is exposed to temperatures of 340–360°F for 2–6 minutes, and then into a flash chamber where it is cooled immediately by vacuum to the malting (conversion) temperature of 145°F. A malt slurry is continuously introduced and the mixture proceeds through the water cooling system to the fermenters.

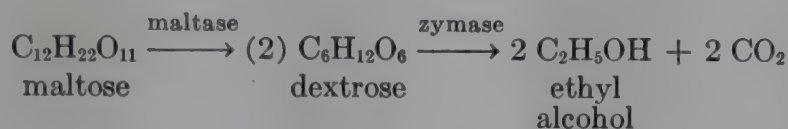
Malt. In the preparation of malt whisky and grain whisky (for Scotch), after mashing is completed, the clear “wort” is drained off, cooled, and transferred to the

fermenter. The suspended residual solids in this case are not permitted to become part of the fermentation process.

FERMENTATION

Beverage alcohol fermentation (qv) involves the conversion of fermentable grain sugars (largely maltose), produced by the action of malt enzymes (amylases) on gelatinized starch, into nearly equal parts of ethyl alcohol and carbon dioxide. This is accomplished by an enzyme complex, *zymase*, which is made available by yeasts, microscopic organisms belonging to the plant kingdom. Yeast multiplies by budding; a new cell is produced about every 70 minutes. Although yeasts of several genera are capable of some degree of fermentation, *Saccharomyces cerevisiae* is almost exclusively used by the distilling industry. It has the ability to reproduce prolifically under normal growth conditions found in distilleries; it has a high fermentation rate and efficiency, and it can tolerate relatively high alcohol concentrations (up to 15–16% by volume). A great variety of strains exist and the characteristics of each strain are evidenced by the type and amount of congeners the yeast is capable of producing. The strain most suitable for a specific purpose can be selected.

Alcoholic fermentation represents a chain of complicated reactions, which can be indicated by the equation



A fermentation efficiency of 95% is obtained based on the sugar available. Of the starch converted to grain sugar and subsequently subjected to fermentation, 5–6% is consumed in side reactions. The extent and type of these reactions depend on (1) yeast strain characteristics; (2) the composition of the wort; and (3) fermentation conditions such as the oxidation–reduction potential, the temperature, and the degree of interference by bacterial contaminants.

Secondary products formed by these side reactions largely determine the characteristics and organoleptic qualities of the final product. In the production of whisky, the secondary products formed and retained during the subsequent operations include a number of aldehydes, esters (such as ethyl acetate), higher alcohols collectively designated “fusel oils,” some fatty acids, phenolics or “aromatics,” and a great many unidentified trace substances. The secondary products retained in the final distillate are known as “congeners.” In the production of grain neutral spirits, the “congeners” are removed from the distillate in a complex multicolumn distillation system. Some distillers, however, retain a small portion of the low-boiling esters in the distillate when the grain neutral spirits are to be matured.

Fermentation of grain mashes is initiated by the inoculation of the set mash with 2–3% by volume of ripe yeast prepared separately (see below) and is characterized by three distinct phases.

(1) *Prefermentation*. Rapid multiplication of yeast from an initial 4–8 million per milliliter to a maximum of 125–130 million per milliliter of the liquid and an increasing rate of fermentation.

(2) *Primary Fermentation*. A rapid rate of fermentation, as indicated by the vigorous “boiling” of the fermenting mash, caused by escaping carbon dioxide. During

this phase secondary conversion takes place—the changing of dextrins to fermentable substances.

(3) *Secondary Fermentation.* A slow and decreasing rate of fermentation. Conversion of the remaining dextrins which are difficult to hydrolyze takes place.

The degree of conversion, agitation of the mash, and the temperature directly affect the fermentation rate. Fermenter mash set at a concentration of 38 gallons of mash per bushel of grain (56 lb) will be fermented to completion in two to five days, depending on the set and control temperatures. The set temperature (temperature of the mash at the time of inoculation) is largely determined by the available facilities for cooling the fermenting mash. If cooling facilities are adequate, temperatures of 80–85°F may be employed; otherwise, the set temperature must be low enough to ensure that the temperature will not exceed 90°F during fermentation. When no cooling facilities are provided, the inoculation temperature must be below 70°F. Excessive temperatures during the prefermentation phase retard yeast growth and stimulate the development of bacterial contaminants which are likely to produce undesirable flavors.

In the production of “sour mash” whisky, federal regulations (U.S.) require that a minimum of 25% of the volume of the fermenting mash must be stillage (cooled, screened liquid recovered from the base discharge of the whisky separating column—pH 3.8–4.1). In addition to producing a heavier-bodied whisky, this procedure provides the distiller with an economical means of adjusting the setting pH (4.8–5.2) to inhibit bacterial development. It also provides buffering action during the fermentation cycle, which is important since secondary conversion will not take place if the fermenting pH drops below 4.1 in the immediate stages. Thin stillage also provides a means of diluting the “cooker” mash to the proper fermenter mash concentration, 30–36 gallons of mash per bushel of grain for the production of spirits, and 38–45 gallons for making whisky.

Preparation of the yeast involves a stepwise propagation; first on a laboratory scale and then on a plant scale to produce a sufficient quantity of yeast for stocking the main mash in the fermenters. A strain of yeast is usually carried in a test tube containing a solid medium (agar slant). A series of daily transfers, beginning with the removal of some yeast from the solid medium, are made into successively larger flasks containing liquid media—diamalt (commercial malt extract) diluted to 15–20° balling, malt extract, or strained sour yeast mash—until the required amount of inoculum is available for the starter yeast mash, called a “dona.” After one day’s fermentation, the dona is added to a yeast mash normally composed of barley malt and rye grains, and representing approximately 2–3½% by weight of the total grain mashed for each fermenter.

The yeast mash is generally prepared by the “infusion mashing” method and then “soured” (acidified) to a pH of 3.9–4.1 by a four to eight hour fermentation with *Lactobacillus delbrueckii* at a temperature of 120–130°F. *Lactobacillus* ferments carbohydrates to lactic acid. Satisfactory souring can be induced with an inoculum of approximately ¼% of culture per volume of mash. The water to meal ratio of 24–28 gallons per bushel attains a yeast mash balling of approximately 21°. Prior to inoculation with yeast, the soured mash is pasteurized to 160–190°F to curtail bacterial activity, then cooled to the setting temperature, 68–72°F.

The sour mash media offers an optimum condition for yeast growth and also has an inhibitory effect on contamination by bacteria. In sixteen hours the yeast cell count reaches 150–250 million per milliliter.

Some distillers use the "sweet yeast" method for yeast development. In this instance the lactic acid souring is not included and the inoculation temperature is usually above 80°F to ensure rapid yeast growth.

DISTILLATION

Distillation involves the separation, selection, and concentration of the alcoholic products of yeast fermentation from the fermented grain mash, sometimes referred to as "fermented wort" or "distillers beer." In addition to the alcohol and the desirable secondary products (congeners), the fermented mash contains solid grain particles, yeast cells, water-soluble proteins, some mineral salts, lactic acid, fatty acids, and traces of glycerol and succinic acid. Although a great number of varieties and degrees of distillation are possible, the most common systems used in the United States are: the continuous whisky separating column with or without an auxiliary doubler unit for the production of straight whiskies; the continuous multicolumn, complex system used for the production of grain neutral spirits; and the batch rectifying column and kettle unit, used primarily in the production of grain neutral spirits which are subsequently stored in barrels for maturation purposes. In the batch system, the heads and tails fractions are separated from the product resulting from the middle portion of the distillation cycle.

Even though most modern plants have various capacity whisky stills available, they find it convenient and flexible to incorporate a whisky separating column into the multicolumn system, thus acquiring a greater range of distillation selectivity—the removal or retention of certain congeners. In the beverage distillation industry, stills and auxiliary piping are generally fabricated of copper, although some stainless steel is used for these purposes. All piping that conveys finished products is tin-lined copper, stainless steel, or glass.

The whisky column, a cylindrical shell which is divided into sections, may contain from 14 to 21 perforated plates, normally spaced 22–24 inches apart. The perforations are usually $\frac{3}{8}$ to $\frac{1}{2}$ inch in diameter and take up about 10% of the plate area. The vapors from the bottom of the still pass through the perforations with a velocity of 20–40 feet per second. The fermented mash is introduced near the top of the still, and passes from plate to plate through down pipes until it reaches the base where the residual mash is discharged. The vapor leaving the top of the still is condensed and forms the product. Some whisky stills are fitted with entrainment removal chambers and also with bubble-cap plate sections—sometimes called "wine" plates—at the top to permit operation at higher distillation proofs. The average whisky still uses approximately 12–15 pounds of steam per proof gallon of beverage spirits distilled. Steam is introduced at the base of the column through a sparger. Where economy is an important factor, a calandria is utilized as the source of indirect heat. The diameter of the still, the number of perforated and bubble-cap plates, the capacity of the doubler, and the proof of distillation are the critical factors that will largely determine the characteristics of a whisky.

The basic continuous complex distillation system for the production of grain neutral spirits usually consists of a whisky separating column, an aldehyde column (selective distillation column), a product concentrating column (sometimes referred to as an "alcohol" or "rectifying" column, from which the product is drawn), and a fusel oil concentrating column. In addition, some distillers in order to secure a greater degree of refinement and flexibility may include one or more of the following: an aldehyde concentrating column (heads concentrating column) and a fusel oil stripping

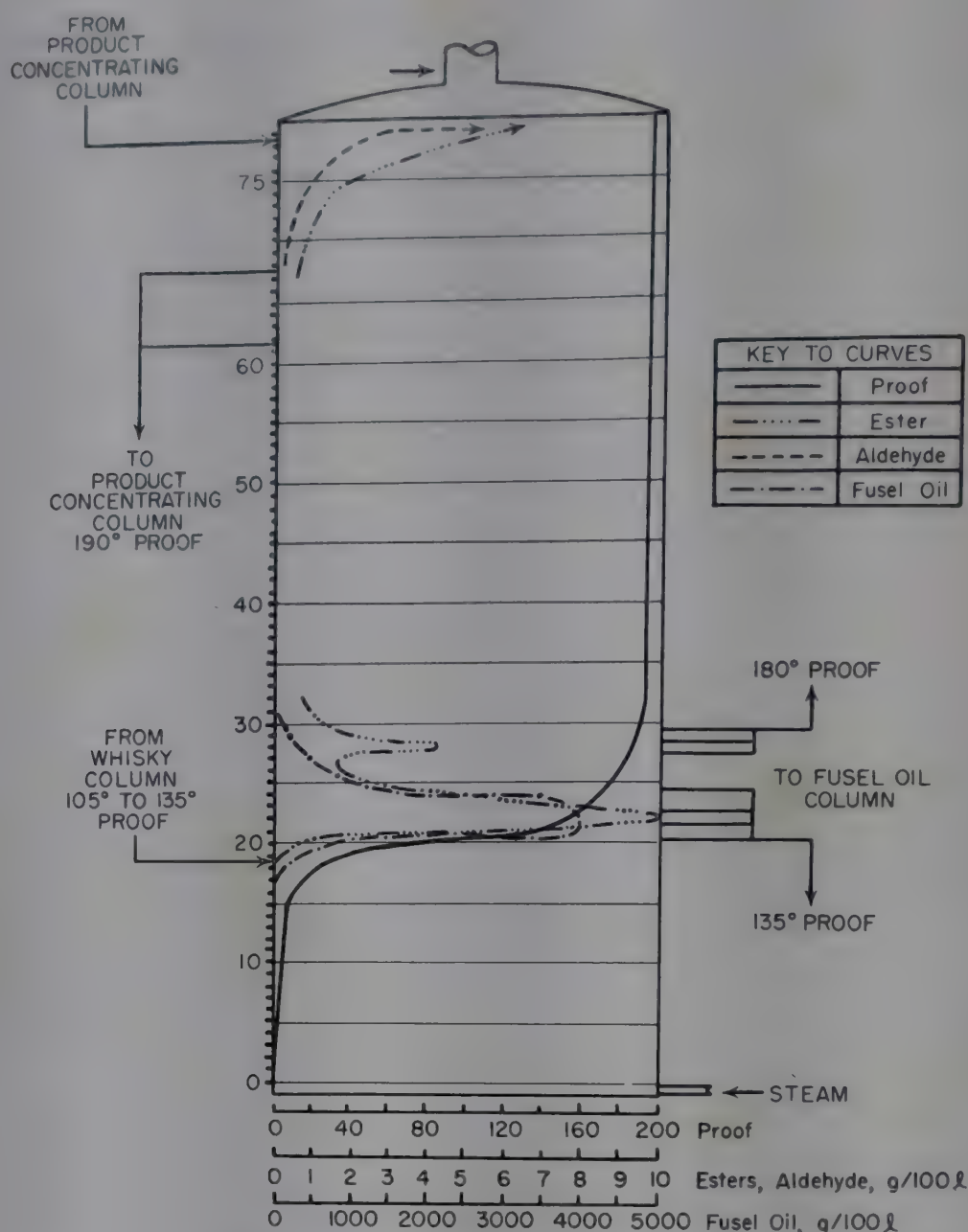


Fig. 4. Selective distillation column.

column. Bubble-cap plates are used throughout the system (except in the whisky column, which may have some bubble-cap plates).

This distillation system offers a wide range of flexibility for the refinement of distilled beverage spirits. Figure 3 shows a five-column, continuous distillation system for the production of grain neutral spirits. A fermented mash (generally composed of 90% corn and 10% barley malt) with an alcohol concentration of approximately 7% by volume is pumped into the whisky column somewhere between the thirteenth and nineteenth perforated plate for stripping. The residual mash is discharged at the base and is pumped to the feed recovery plant; the overhead distillate (ranging in proof from 105–135°) is fed to the selective distillation column (also called the “aldehyde” column), which has over 75 bubble-cap plates. The main stream (20–40° proof) from the selective distillation column (as illustrated in Figure 3) is pumped to the product concentrating column. A heads draw (aldehydes and esters) from the condenser is pumped to the heads concentrating column (also called the “aldehyde concentrating” column), and a fusel oil and ester draw is pumped to the fusel oil concentrating column. The product is withdrawn from the product concentrating column.

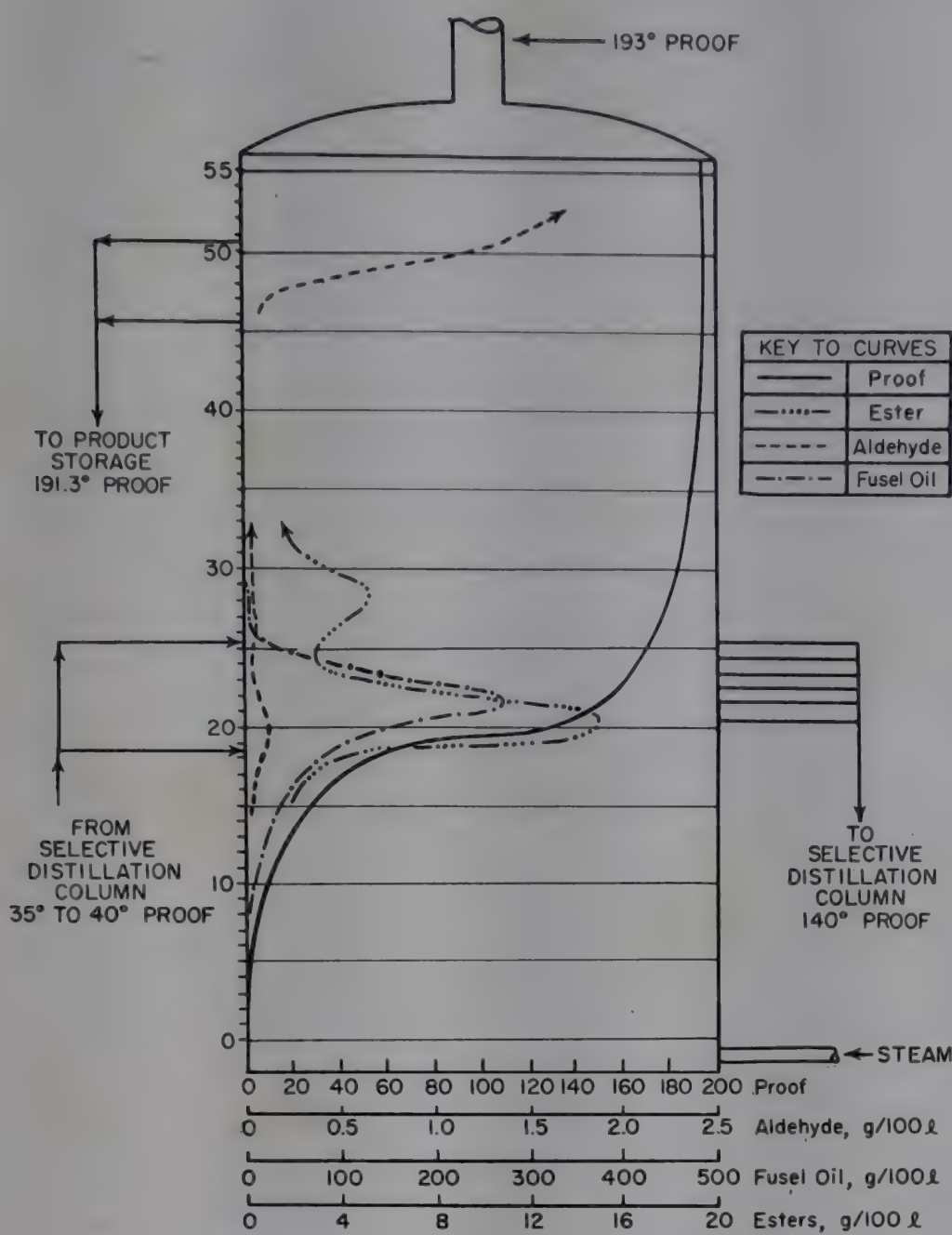


Fig. 5. Product concentrating column.

Some accumulation of heads, at the top of the product concentrating column, are removed at the condenser, and transferred to the aldehyde concentrating column. The function of the aldehyde concentrating column is to remove the heads from the system for disposal. The fusel oil concentrating column removes the fusel oil from the system. Figures 4, 5, and 6 show the distribution and concentration of alcohols and congeners through the selective distillation column, the product concentrating column, and the heads concentrating column. These figures correspond to operating the system not exactly as shown in the flowsheet, but in such a manner that the discharge from the selective distillation column is at 0° proof.

By-Products. The discharge from the base of the whisky column is called “stillage” and contains in solution and in suspension substances derived from grain (except the starch which has been fermented), and from the mashing and fermentation processes. The suspended solids are recovered by screening and then subjected to a pressing and a drying operation (dehydrating), usually in rotary, steam-tube dryers. The liquid portion, called “thin stillage,” is concentrated by a multieffect evaporator to a syrup with a solid content of 30–35%. This concentrate can either be mixed

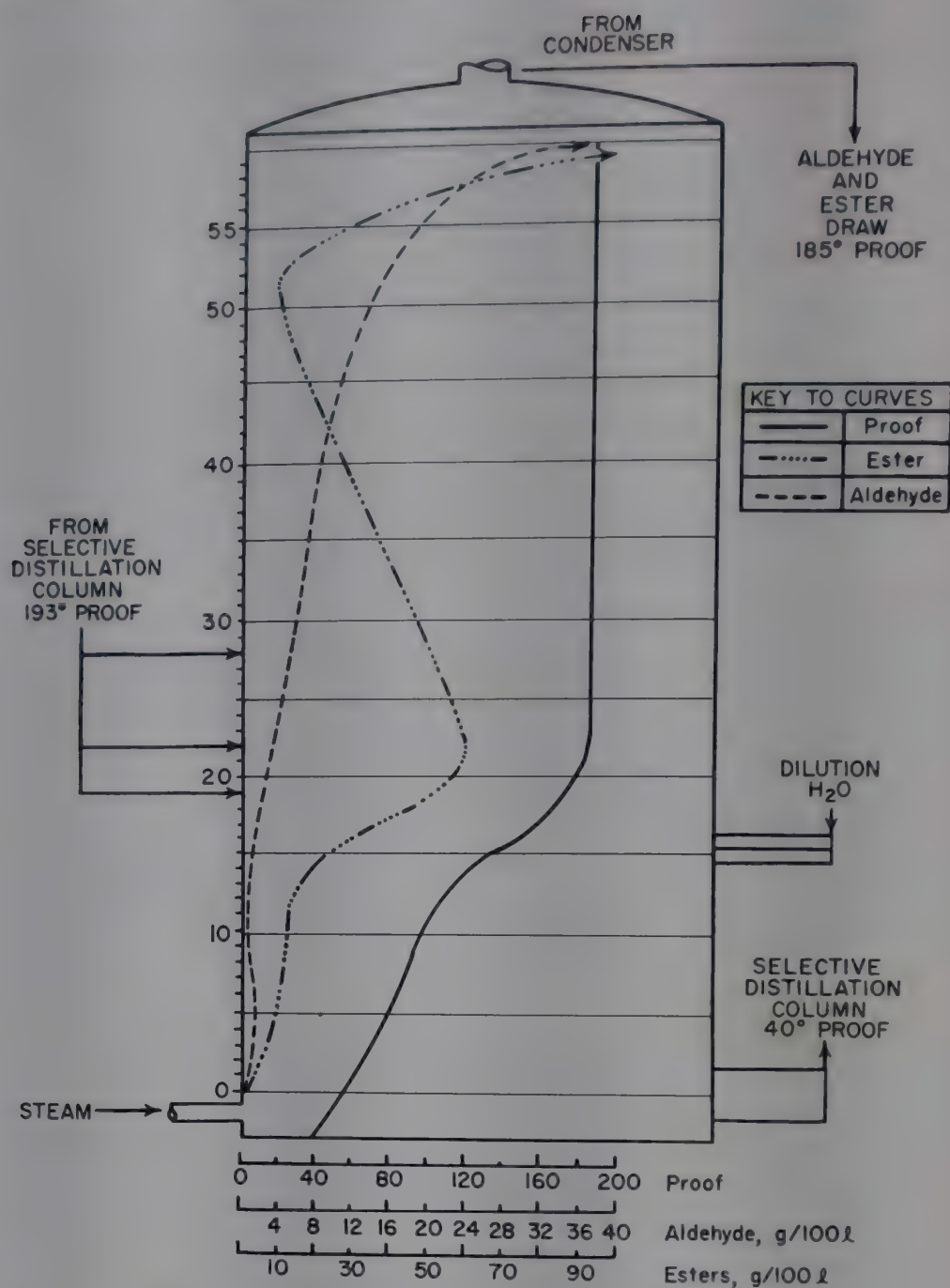


Fig. 6. Aldehyde (heads) concentrating column.

with the previously screened-out solids and the two dried together, or it can be dried separately on rotary-drum dryers. The by-products are known as *distillers feeds* and are used by the feed industry to fortify dairy, poultry, and swine formula feeds. Distillers feeds are rich in proteins (24–35%), fat (8%), choline, niacin, and other B complex vitamins, and contain vital fermentation growth factors that produce good growth responses in livestock and poultry.

MATURATION

In the United States, the final phase of the whisky production process is called maturation and involves the storage of beverage spirits (which at this point are colorless and rather pungent in taste) in new, white oak barrels, whose staves and heading are charred. The duration (years) of storage in the barrel depends on the time it takes a particular whisky to attain the desirable ripeness or maturity. The staves of the barrel may vary in thickness from $\frac{3}{4}$ to $1\frac{1}{8}$ inch. The outside dimensions of a barrel that will hold approximately 50 U.S. gallons are: height, approximately 34 $\frac{1}{2}$ inches,

and diameter at the head, approximately $21\frac{1}{4}$ inches. Storage facilities for barrels of whisky are called warehouses. They vary in construction from brick and mortar types, single and multiple floors (as many as six) having capacities up to 100,000 barrels, to wooden sheet-metal-covered buildings (called "iron clads"), generally not exceeding 30,000 barrels capacity. It is customary in the industry to provide some means of natural ventilation. As the whisky reposes in the barrel it is subject to critical factors which will largely determine its course of change and its final outcome. The thickness of the stave, the depth of the char (controlled by regulating the duration of the firing, 30–50 seconds), the atmospheric conditions of temperature and humidity, the entry proof, and, finally, the length of storage impart definite and intended changes in the aromatic and taste characteristics of a whisky. Where warehousing conditions are not controlled, the maturing process is subject to the natural variations resulting from changes in climatic conditions. It is generally agreed that the changes in the maturing whisky are caused by three principal types of reactions occurring simultaneously and continually in the barrel: (1) extraction of complex wood constituents by the liquid; (2) oxidation of the original components in the liquid and other material extracted from the wood; and (3) reaction between the various organic substances present in the liquid, resulting in the formation of new congeners.

Comprehensive studies involving the changes occurring during the maturation of whisky have been published by four groups of investigators: Crampton and Tolman (2), Valaer and Frazier (5), Liebmann and Rosenblatt (3), and Liebmann and Scherl (4). Although these reports contain detailed information on the concentration of various congeners throughout the course of the maturation period, little is revealed of the interrelationships between various congeners except for the nonvolatile groups, such as solids, nonvolatile acids, tannin, and color. Notable among the observed changes are increases in the concentrations of acids, esters, and solids. Based on the average data in the summary tables of each study, it is revealed that there exists throughout the maturation period a linear relationship between the increase in acids and esters and the increase in dissolved solids; this suggests that the formation of acids and esters is directly dependent upon some precursor which is extracted from the barrel at the same rate as the bulk of the solid fraction (6). The progress of maturing of a type of bourbon as measured by the principal ingredients is illustrated in Table 4. It is evident that the congeners amount to only about $\frac{1}{2}$ – $\frac{3}{4}\%$ of the total weight. Yet it is this small fraction which determines the quality of the final product. Consequently, there can be a wide variation in the taste and aroma of matured whiskies, simply because of the wide variation in the concentration of their congeners. For example, esters may vary from 8.0–18.0 g/100 liters, and aldehydes from 0.7–7.6 g/100 liters. Nevertheless, there is no correlation between chemical analysis and quality; ie, taste and aroma. It is necessary to rely on human senses of smell and taste to detect the fine variations and thus evaluate the quality of whiskies.

Present analytical results are expressed in terms of one component for each chemical class; ie, acetic acid for acids, acetaldehyde for aldehydes, etc. However, more refined techniques of analysis are being applied to a systematic breakdown of the congener groups to their individual components. Until the advent of gas chromatography long and tedious chemical procedures were generally required for separation of the congeners. Distillation, countercurrent distribution, and other physical methods were utilized to effect concentration of various congener groups. These concentrates were reacted to form chemical derivatives which were then subjected to further

Table 4. Changes Taking Place in Bourbon Whisky Stored in Wood (3)

Age, years	Range	Proof	Extract ^a	Acids ^a	Esters ^a	Alde- hydes ^a	Fur- fural ^a	Fusel oil ^a	Color
new	av	101.0	26.5	10.0	18.4	3.2	0.7	100.9	0.0
	max	104.0	161.0	29.1	53.2	7.9	2.0	171.3	0.0
	min	100.0	4.0	1.2	13.0	1.0	trace	71.3 42.0	0.0
1	av	101.8	99.4	41.1	28.6	5.8	1.6	110.1	7.1
	max	103.0	193.0	55.3	55.9	8.6	7.9	173.4	10.9
	min	100.0	61.0 54.0	24.7 10.4	17.2 10.4	2.7	trace	58.0 42.8	5.4 4.6
2	av	102.2	126.8	45.6	40.0	8.4	1.6	110.1	8.6
	max	104.0	214.0	61.7	59.8	12.0	9.1	197.1	11.8
	min	100.0	81.0 78.0	25.5 23.5	24.4 11.2	5.9	0.4	86.2 42.8	6.9 5.7
4	av	104.3	151.9	58.4	53.5	11.0	1.9	123.9	10.8
	max	108.0	249.0	73.0	80.6	22.0	9.6	237.1	14.8
	min	100.0	101.0 92.0	40.0 40.0	28.2 13.8	6.9	0.8	95.0 43.5	8.6 7.4
6	av	107.9	185.1	67.1	64.0	11.9	1.8	135.3	13.1
	max	116.0	287.0	81.0	83.9	23.3	9.5	240.0	17.5
	min	102.0	132.0 127.0	53.6 45.0	36.4 17.9	7.7	0.9	98.1	12.0 9.8
8	av	111.1	210.3	76.4	65.6	12.9	2.1	143.5	14.2
	max	124.0	326.0	91.4	93.6	28.8	10.0	241.8	20.9
	min	102.0	152.0 141.0	64.1 53.7	37.7 22.1	8.7	1.0	110.0 47.6	12.3 10.5

^a Grams per 100 liters of proof spirit.

separation. Paper and column chromatography have been used extensively for this work. After separation of the components, identification is possible by infrared and mass spectrometry.

It is now possible with the high sensitivity (flame and β -ray ionization detection) and efficiency available with gas chromatographic techniques to present a qualitative profile of alcoholic distillates without prior treatment of sample. One technique, flame ionization, involves the use of a hydrogen flame, for the combustion of organic substances, to produce electrons and negative ions which are collected on an anode. The resulting electrical current is proportional to the amount of material burned. The other, β -ray ionization, involves the use of beta particles emitted from a source such as strontium-90 to ionize the carrier gas and components in it. The measure of the electrical current, resulting from the collection of electrons on the anode, is used in the determination or detection of the substance. This may augment sensory evaluations. A positive identification of the separated congeners can be made by infrared and mass spectrometers.

Another field of microanalysis, Nuclear Magnetic Resonance (NMR), offers the organic chemists new methods in the identification of organic substances. It makes use of a number of physical methods which measure nuclear properties, such as spin numbers and nuclear magnetic moments, to identify the structure of an organic com-

pound. This technique may offer possibilities in the identification of congeners present in alcoholic beverages.

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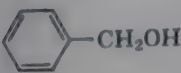
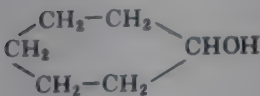
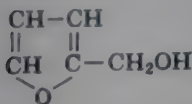
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ALCOHOLS

Alcohols can be regarded as hydroxyl (OH) derivatives of hydrocarbons. In general, the characteristic properties of an alcohol are not displayed unless the hydroxyl group is attached to a carbon atom which is itself linked by single bonds to other atoms. Compounds in which a hydroxyl group is directly attached to an aromatic nucleus have decidedly different properties, and are referred to as phenols (see Phenol and phenols). However, benzyl alcohol, for example, is classified as a typical aromatic alcohol since the hydroxyl is separated from the benzene ring by a methylene group. Examples of the different types of alcohols are given in Table 1.

Table 1. Different Types of Alcohols

Formula	Name	General type
$\text{CH}_3\text{CH}_2\text{OH}$	ethyl alcohol	aliphatic alcohol (saturated)
$\text{CH}_2=\text{CHCH}_2\text{OH}$	allyl alcohol	aliphatic alcohol (unsaturated)
	benzyl alcohol	aromatic alcohol
	cyclohexanol	alicyclic alcohol
	furfuryl alcohol	heterocyclic alcohol

Alcohols are discussed in the following articles: Methanol; Ethanol; Propyl alcohols; Butyl alcohols; Amyl alcohols; Cyclohexanol; Benzyl alcohol; Nitro alcohols; Alcohols, higher, fatty; Alcohols, higher, synthetic; Alcohols, polyhydric; Alcohols, unsaturated; Glycols; Glycerol.

According to the number of hydroxyl groups they contain, alcohols are called monohydroxy, dihydroxy, trihydroxy, and polyhydroxy (the terms monohydric, dihydric, etc, are also frequently employed). Dihydroxy alcohols are often referred to as glycols. In general, more than one hydroxyl group cannot be attached to the same carbon atom since compounds containing such a structure usually lose water. Thus 1,1-dihydroxyethane, $\text{CH}_3\text{CH}(\text{OH})_2$, when formed is at once converted to acetaldehyde, CH_3CHO . However, there are a few exceptions to this rule, as for example, chloral hydrate, $\text{CCl}_3\text{CH}(\text{OH})_2$ (see Chloral).

Alcohols are classified as primary, secondary, or tertiary, depending upon how many hydrogen atoms are attached to the carbon atom holding the hydroxyl group. If two hydrogen atoms (or three in methanol) are attached to the carbon atom holding the hydroxyl group, the alcohol is primary; if one hydrogen is attached to the carbon atom, the alcohol is secondary; if no hydrogen is attached, the alcohol is tertiary. The use of these terms is best illustrated by reference to the butyl alcohols in Table 2.

Table 2. The Different Classes of Butyl Alcohols


Name	Structure	Class	Characteristic group
<i>n</i> -butyl alcohol	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	primary	$-\text{CH}_2\text{OH}$
isobutyl alcohol	$(\text{CH}_3)_2\text{CHCH}_2\text{OH}$	primary	$-\text{CH}_2\text{OH}$
<i>sec</i> -butyl alcohol	$\text{CH}_3\text{CH}_2\text{CHOHCH}_3$	secondary	$-\text{CHOH}$
<i>tert</i> -butyl alcohol	$(\text{CH}_3)_3\text{COH}$	tertiary	$-\text{COH}$

Nomenclature

Alcohols are named in three different ways: (1) Common names—these names usually contain the word alcohol and are based either on natural sources or on the hydrocarbon from which the radicals attached to the hydroxyl group are derived; ethyl alcohol, *n*-decyl alcohol, cetyl alcohol (see Table 3). The term iso is used to describe certain primary aliphatic alcohols which possess a terminal $(\text{CH}_3)_2\text{CH}-$ group but which do not have any other branched chains present in the molecule. The

use of the term is limited to isopropyl, isobutyl, and isoamyl alcohols. The term is also often used to denote “branched chain”; commercial “isooctyl alcohol” is a mixture of branched C₈ alcohols. (2) IUPAC or IUC names—this system of naming alcohols follows the rules laid down by the International Union of Pure and Applied Chemistry (formerly the International Union of Chemistry) and is based on the original Geneva system first proposed in 1892. According to the IUPAC rule, the name of the alcohol is derived from the name of the hydrocarbon corresponding to the longest straight chain (ie, the longest unbranched chain) containing the alcohol function, by dropping the final “e” and adding the suffix “ol” (or “diol,” “triol” etc, according to the number of OH groups). The position of the OH group is indicated by the lowest

Table 3. The Nomenclature of Alcohols

Formula	Common name	IUPAC (IUC)	Methanol name ^a
CH ₃ CH ₂ CH ₂ CH ₂ OH	<i>n</i> -butyl alcohol	1-butanol	<i>n</i> -propylmethanol ^b
CH ₃ (CH ₂) ₈ CH ₂ OH	<i>n</i> -decyl alcohol	1-decanol	<i>n</i> -nonylmethanol ^b
CH ₃ (CH ₂) ₁₄ CH ₂ OH	cetyl alcohol	1-hexadecanol	
CH ₃ CH=CHCH ₂ OH	crotyl alcohol	2-butene-1-ol	
CH ₂ OHCH ₂ OH	ethylene glycol	1,2-ethanediol	
(C ₆ H ₅) ₃ OH			triphenylmethanol
 -CH ₂ OH	3-pyridylmethyl alcohol		3-pyridinemethanol

^a Prior to 1957 these were usually called carbinols.
^b Methanol names are not normally used for simple alcohols of this type.

possible number; thus, 1-butanol for CH₃CH₂CH₂CH₂OH, 2-butanol for CH₃CH₂-CHOHCH₃. (The position of the numeral in the name is not standardized; this encyclopedia follows United States practice; in Great Britain the numeral is placed immediately before the syllable to which it refers, thus butan-1-ol; in Germany the forms butanol-1 or butanol(1) are often used.) For unsaturated alcohols the locant for the hydroxyl is placed immediately before “-ol,” as 2-buten-1-ol (see Table 3). (3) Methanol names—these names (previously termed carbinols) are used (a) for certain derivatives of methanol where all of the hydrogen atoms in the methyl group are replaced by radicals, as for example, triphenylmethanol (formerly triphenylcarbinol); (b) for certain aromatic and heterocyclic alcohols which can be considered to be derivatives of methanol, as with 3-pyridinemethanol.

The relation between the common name and the IUPAC name is sometimes deceptive. Thus the expression “butyl alcohols” covers the four alcohols C₄H₉OH as shown in Table 2. But in the IUPAC system the expression “butanol” denotes an alcohol with four carbon atoms in the longest straight chain containing the functional group. Thus isobutyl alcohol, (CH₃)₂CHCH₂OH, is 2-methyl-1-propanol (although it is sometimes incorrectly referred to as “isobutanol”). Similarly, isopropyl alcohol is 2-propanol (not “isopropanol”), and isoamyl alcohol is 3-methyl-1-butanol.

If the molecule also contains another functional group having precedence over the hydroxyl group according to the rules of nomenclature, the alcoholic group must be expressed as a prefix. In these cases the term “hydroxy” is used, eg, 3-hydroxypropionic acid, HOCH₂CH₂COOH.

Physical and Chemical Properties

The alcohols are clear liquids or colorless solids; most of the monohydroxy alcohols are lighter than water and all are soluble in organic solvents. The lower aliphatic alcohols are mobile liquids; the viscosity increases with the molecular weight so that the alcohols C_6 to C_{11} become increasingly viscous. *n*-Dodecyl alcohol is the first solid member of the series of normal primary alcohols. Cyclohexanol is a solid, whereas benzyl alcohol is a liquid heavier than water. Alcohols containing two and three hydroxyl groups are viscous, colorless, sweet-tasting liquids, and the higher polyhydroxy alcohols are mostly crystalline solids.

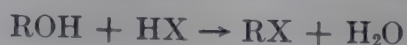
All alcohols containing one to three carbon atoms are miscible with water in all proportions, but *n*-butyl, *sec*-butyl, and amyl alcohols have only limited solubility in water. In fact, the solubility falls off so rapidly with increasing molecular weight that the hexyl and higher alcohols are essentially insoluble. Two structural effects should be noted; with alcohols of the same molecular weight, increased branching results in increased solubility in water and the solubility increases from the primary to the secondary to the tertiary alcohol. Thus, for example, whereas *n*-butyl alcohol has limited solubility in water, *tert*-butyl alcohol is completely miscible with water. The introduction of additional hydroxyl groups also increases the solubility in water appreciably and decreases the solubility in ether and alcohol.

The boiling points of the alcohols are considerably higher than would be predicted on the basis of molecular weight alone. This is due to hydrogen bonding between the hydroxyl groups. From ethyl alcohol to higher primary unbranched alcohols the boiling points increase with surprising regularity, the rise being about 20°C per methylene group. For alcohols of a given molecular weight, the boiling point decreases with increased branching and also decreases from primary to secondary to tertiary.

The physical and chemical properties of the alcohols are primarily dependent upon the hydroxyl group but the position of the hydroxyl group in the molecule as well as the nature of the hydrocarbon radical may alter these properties. The properties may be further influenced by the presence of other functional groups, eg, a double bond or triple bond (see Alcohols, unsaturated); amine (see Alkanolamines); carboxy (see Lactic acid; Tartaric acid); chlorine (see Chlorohydrins); cyano (see Cyano-hydrins); nitro (see Nitro alcohols). (See also Carbohydrates; Sterols; Sugars.)

Reactions

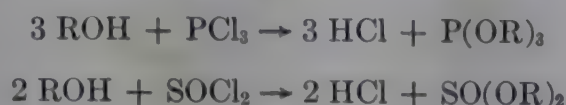
The hydroxyl group may be replaced by halogen to form alkyl halides. This transformation may be effected by a variety of reagents, among which the halogen acids, the phosphorus tri- and pentahalides, and thionyl chloride are most useful.



The ease of replacement is markedly affected by the position of the hydroxyl group, the order of increasing reactivity being primary, secondary, tertiary. The halogen involved also influences the rate of reaction, and, in general, iodides may be prepared more readily than bromides, which in turn may be prepared more readily than chlorides. Although a number of low-molecular halides are now prepared by direct halo-

genation of the parent hydrocarbons, the replacement of hydroxyl by halogen is still important for the preparation of high-molecular halides.

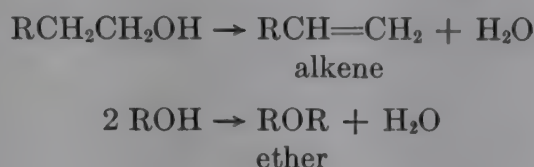
Under appropriate conditions, the phosphorus halides and thionyl chloride react with alcohols in a different manner to give alkyl phosphites and sulfites, respectively.



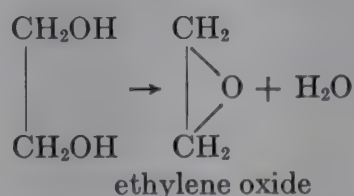
Phosphorus trichloride usually reacts with primary alcohols to give phosphites while phosphorus tribromide gives mostly alkyl halides. Secondary alcohols normally react to give both products while tertiary alcohols invariably form alkyl halides.

The replacement of the hydroxyl group by an amino group, though not an important reaction in the aliphatic series, is important in the preparation of some aromatic amines (see Ammonolysis).

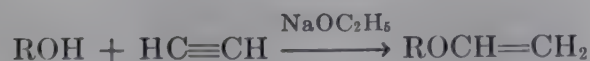
The dehydration of alcohols may proceed intramolecularly to produce alkenes (olefins) or intermolecularly to form ethers. Generally both alkene and ether,



are formed to some extent at the same time, but the conditions may be altered to favor one reaction or the other. The most important factor is temperature, higher temperatures favoring the formation of alkenes. Alcohols are dehydrated smoothly to alkenes by passing them over a prepared alumina or silica catalyst heated to 350–450°C. The actual conditions are modified in accordance with the useful rule that tertiary alcohols are more easily dehydrated than primary alcohols. Secondary alcohols are usually intermediate in this respect. This procedure is suitable for the industrial or laboratory synthesis of alkenes and may also be extended to the dehydration of diols to diolefins. A useful catalyst for the laboratory dehydration of alcohols is 48% hydrobromic acid. Glycols and polyhydroxy alcohols tend to form cyclic ethers or alkylene oxides.



The addition of alcohols to acetylene in the presence of alkaline catalysts leads to vinyl ethers.

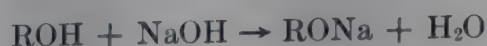


The acid-catalyzed addition of alcohols to acetylene or to a vinyl ether results in acetals (qv) or diethers of acetaldehyde. Generally acetals, RCH(OR')_2 , are formed by condensation of alcohols with aldehydes.

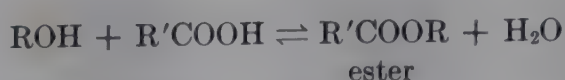
The hydrogen atom of the hydroxyl group of alcohols may be replaced by an active metal, such as sodium, potassium, or calcium, with the formation of a metal alkoxide and the evolution of hydrogen gas.



Magnesium and aluminum also react to form alkoxides, but the reaction must be catalyzed, as by amalgamating the metal. There is a marked decrease in reactivity of the hydroxyl hydrogen in proceeding from primary to secondary to tertiary alcohols, and indeed the reaction with tertiary alcohols must be forced by increasing the temperature and lengthening the reaction time. Alkoxides such as sodium ethoxide and aluminum isopropoxide (see Alkoxides, metal) are used in organic syntheses as condensing or reducing agents. Alcoholic alkali, made by dissolving caustic alkalies in alcohol, contains some alkoxide.

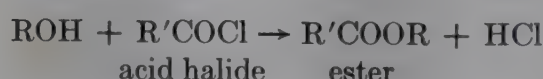
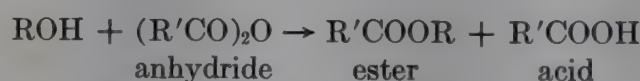


Organic esters are formed by the elimination of water between an alcohol and an organic acid.

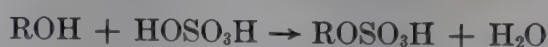
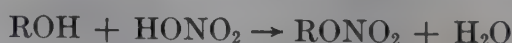


The reaction is reversible and reaches equilibrium slowly. Ordinarily the catalyst used is acidic. The customary methods of driving the reaction to completion are (1) removal of water as an azeotrope; (2) use of a large excess of alcohol; or (3) use of a large excess of acid (see Esterification; Esters, organic). The esterification is not entirely analogous to the neutralization of acids by bases, since the latter is an ionic reaction and proceeds "instantaneously," while ester formation proceeds slowly. The rate of esterification is also influenced by the position of the hydroxyl groups in the chain. Primary and secondary alcohols can be prepared by acid-catalyzed esterification, but tertiary alcohols are essentially dehydrated under these conditions.

Esters may also be prepared by reaction of alcohols with acid anhydrides or acid halides. Both of these reactions are irreversible and are used when the alcohol or the acid is valuable.



Alcohols also form esters with inorganic acids, such as nitric or sulfuric acid.



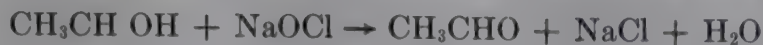
The dehydrogenation of primary alcohols to aldehydes and of secondary alcohols to ketones may be effected by passing the alcohol vapors over a heated dehydrogenation catalyst, such as reduced copper.



Alcohols differ greatly in their behavior toward oxidizing agents. Primary alcohols are oxidized to aldehydes and acids; secondary alcohols are oxidized to ketones; tertiary alcohols in neutral or alkaline solution are stable toward oxidizing agents, but in acid solution are dehydrated to alkenes, which are oxidized with breaking of the carbon chain. This behavior of the three types of alcohols may be employed to distinguish between them.



Ethyl alcohol reacts rapidly with sodium hypochlorite to give chloroform, an example of the *haloform reaction*. The sequence of reactions is as follows:



Similarly, bromoform (CHBr_3) and iodoform (CHI_3) are obtained from sodium hypobromite and hypoiodite, respectively. Ethyl alcohol is the only primary alcohol which gives the haloform reaction. However, methyl ketones (for example, acetone) undergo the reaction and also those secondary alcohols which can be oxidized to methyl ketones (those containing a terminal $-\text{CHOHCH}_3$, eg, isopropyl alcohol).

Characterization. Alcohols can be characterized by formation of solid esters, such as the *p*-nitrobenzoates and the 3,5-dinitrobenzoates. These esters are usually prepared through the reaction of the appropriate benzoyl chloride with the alcohol in the presence of pyridine. The method is applicable to all three classes of alcohols.



Primary and secondary alcohols can also be characterized by means of their carbamates or urethans, formed by the reaction of the alcohol with a suitable aryl isocyanate. Among the isocyanates commonly used should be mentioned α -naphthyl-, *m*- and *p*-nitrophenyl-, and 3,5-dinitrophenyl isocyanates.



Tertiary alcohols are usually dehydrated to olefins by isocyanates and consequently cannot normally be characterized by these reagents.

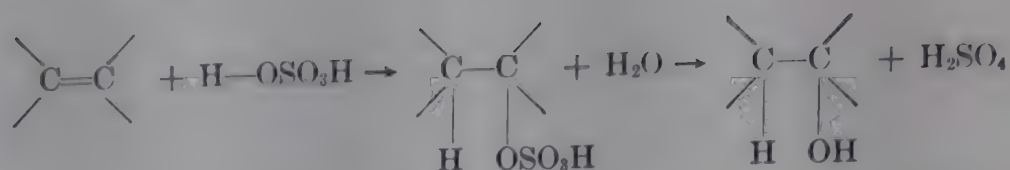
Natural Sources

Alcohols, as such, occur widely in nature in volatile oils (see Oils, essential) and also as esters in volatile oils, fats (qv), fatty oils, and waxes (qv). Among the more important naturally occurring alcohols are those obtained from esters, and of these, probably glycerol, 1,2,3-trihydroxypropane, is the most important. The chief alicyclic alcohols are found in plant and animal tissues (see Sterols). The best-known substituted alcohols are the sugars, which are aldehydo or ketopolyhydroxy compounds (see Carbohydrates; Sugars).

Preparation

The synthesis of industrially important alcohols depends in general upon a number of special reactions. A brief description of the most important reactions follows.

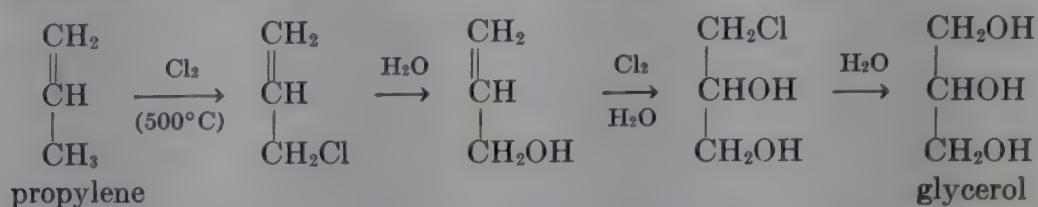
Hydration of Alkenes. In this reaction the negative $-\text{OSO}_3\text{H}$ radical adds to the carbon atom holding the fewest number of hydrogen atoms (Markownikoff's rule), so that secondary and tertiary alcohols are generally obtained (except for ethanol). The alcohols which are prepared commercially by this method are ethanol, 2-propanol, 2-butanol, and 2- and 3-pentanol (see Ethanol; Amyl alcohols; Butyl alcohols; Propyl alcohols).



Hydrolysis of Halides and Sulfates. This synthetic method is applicable to the preparation of primary and secondary alcohols; tertiary halides are dehydrohalogenated to a large extent. Some of the butyl and amyl alcohols are made in this way.



A special application is the synthesis of glycerol starting with propylene.



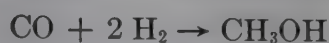
The key step in this synthesis is the chlorination of propylene at high temperatures to give allyl chloride rather than addition products.

Hydrolysis of Organic Esters. The hydrolysis is catalyzed by both acids and bases, the acid-catalyzed reaction being reversible. It is of considerable commercial importance for the production of alcohols from naturally occurring esters.



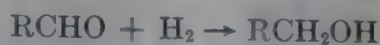
Oxidation of Hydrocarbons. The oxidation of natural gas under very carefully controlled conditions gives a complex mixture of alcohols, aldehydes, and acids. Methanol, ethanol, and C_3 and C_4 alcohols are among those that can be formed. Some methanol, together with other products, is made commercially by this reaction (see Hydrocarbon oxidation).

Reduction of Carbon Monoxide. The formation of methanol (qv) from the reaction of carbon monoxide with hydrogen is a very important commercial process.



Temperatures in excess of 300°C and pressures of at least 270 atm are usually employed. Oxides of zinc, chromium, and copper are often used as catalysts. Under suitable conditions the yield of methanol is almost 100 percent. Higher alcohols can also be obtained from carbon monoxide and hydrogen under suitable conditions and the resultant reaction is called the *oxyl process* (see Carbon monoxide-hydrogen reactions).

The Oxo Process. Hydrogen and carbon monoxide react with olefins in the presence of cobalt carbonyls (at about 150°C and 200 atmospheres) to give primarily aldehydes.



Thus propylene reacts to give normal and iso butyraldehydes (see equation). The resultant aldehydes are then reduced to the corresponding alcohols—some alcohols are also formed directly in the oxo process (qv). The oxo reaction is more accurately termed *hydroformylation* since it involves the addition of a molecule of CO and H_2 .

Reduction of Aldehydes and Ketones. The reduction of aldehydes and ketones to alcohols can be carried out using sodium and alcohol.



Lithium aluminum hydride, LiAlH_4 , (see Hydrides) is a particularly valuable reducing agent and is frequently used in the laboratory (see also the following section). Sodium borohydride, NaBH_4 , can also reduce aldehydes and ketones and has the additional advantage that it can be used in aqueous solutions.

Reduction of Acids. The carboxylic acids are smoothly reduced by lithium aluminum hydride in the laboratory. Ether is commonly used as a solvent.



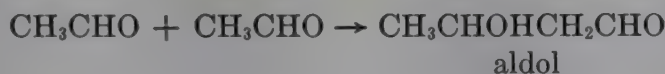
Acid chlorides and anhydrides are also reduced to alcohols by this reagent.

A number of higher alcohols are manufactured by reduction of fatty acids (in the form of their glycerides or simple esters) either with sodium or by high-pressure hydrogenolysis (see Alcohols, higher, fatty).

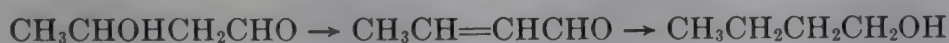
Reduction of Esters. The reduction of esters by alkali metals in alcohols or by high-pressure hydrogenation over copper oxide–chromium oxide has been used both in the laboratory and on an industrial scale. The hydrogenation of the higher fatty esters is the most important technological application. Lithium aluminum hydride can also be used.



Aldol Condensation. Acetaldehyde, under the influence of mild alkali or acid, condenses to form aldol.



Aldol readily dehydrates to crotonaldehyde, which can be reduced to 1-butanol.

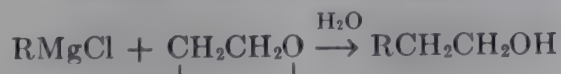


Other aldehydes undergo the same condensation, giving β -hydroxyaldehydes, which can be referred to collectively as aldols. Aldols can be reduced to 1,3-glycols.

The Grignard Reaction. The Grignard reaction (qv) involves the addition of an alkyl(or aryl)magnesium halide to an aldehyde, ketone, ester, or alkene oxide.



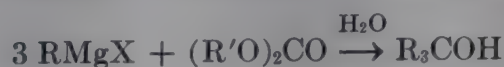
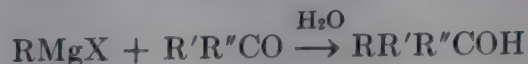
Although this synthesis is not generally used industrially, it does afford a method of preparing primary, secondary, and tertiary alcohols, which may not be available by other means. Primary alcohols containing one or two carbon atoms more than the organic halide are prepared by adding the organomagnesium halide to formaldehyde or to ethylene oxide, respectively.



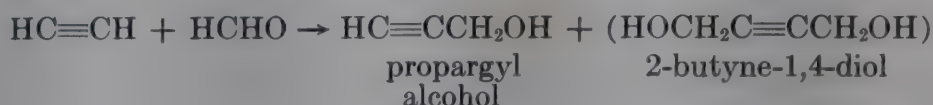
Secondary alcohols are obtained from an aldehyde (except formaldehyde).



Tertiary alcohols are obtained from ketones, esters, and dialkyl carbonates.

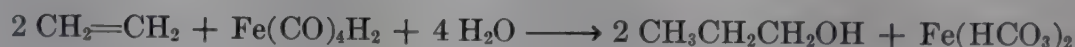


Addition of Aldehydes or Ketones to Acetylene. A number of acetylenic alcohols (mono- and dihydroxy) can be synthesized by this reaction, using a copper acetylide catalyst.



These acetylenic alcohols can be hydrogenated to the corresponding saturated alcohols (see Alcohols, unsaturated).

Addition of Ethylene to Metallic Carbonyl Compounds. The equation shows the formation of 1-propanol from ethylene and iron carbonyl hydride.



Fermentation of Carbohydrates. A number of industrial alcohols are obtained by fermentation procedures. Ethyl and *n*-butyl alcohols are probably the most important of these, although 2,3-butanediol and two of the amyl alcohols have also been obtained in this way (see the individual alcohols; Glycols).

Use of Trialkylaluminum Compounds. By a process developed by Karl Ziegler and co-workers it is now possible to prepare any of the straight-chain, even-carbon, primary alcohols from olefins. (This is in contrast to the addition of water or acids to the olefins, which lead to secondary or tertiary alcohols.)

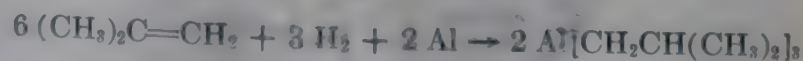
Aluminum is reacted with hydrogen and ethylene to give triethylaluminum.



Reaction with ethylene under high pressure lengthens the alkyl chains to $-(\text{CH}_2-\text{CH}_2)_n\text{H}$.

Reaction with oxygen leads to the insertion of an oxygen atom between the aluminum and carbon, giving aluminum alkoxides, $\text{Al}(\text{OR})_3$, which can then be hydrolyzed to the primary alcohols. For the commercial development of this process, see Alcohols, higher, synthetic.

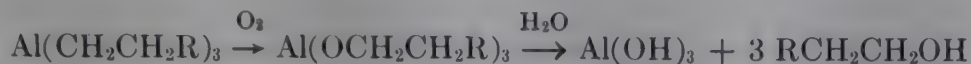
A variation of the process involves the reaction of isobutylene with hydrogen and finely divided aluminum at about 150°C and 200 atmospheres (in the absence of oxygen) to give triisobutylaluminum.



Triisobutylaluminum can react at 100°C with other olefins having a terminal double bond to give new trialkylaluminum compounds.



The three alkyl groups are then oxidized to alkoxy groups followed by hydrolysis of the latter to give primary alcohols.



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ALCOHOLS, HIGHER, FATTY

The term "higher alcohols" generally refers to the class of monohydric aliphatic alcohols containing six or more carbon atoms. Higher alcohols derived from natural products, ie, fats, oils, and waxes, are usually referred to as "fatty alcohols." These alcohols are the subject of this article.

Higher alcohols are also manufactured by various synthetic routes. These are described in the following article, Alcohols, higher, synthetic.

The fatty alcohols are predominantly straight-chain primary alcohols, usually with an even number of carbon atoms. Some of these can also be manufactured synthetically, but many other synthetic higher alcohols have more or less highly branched chains.

The majority of natural fats and oils consist of fatty triglycerides, ie, glycerol esterified with 3 mols of a fatty acid. These constitute the largest source of natural raw materials for the production of fatty alcohols, which are obtained by reduction of the fatty acids (see below under Manufacture). The fatty acid portions of the triglycerides are randomly mixed with respect to chain length and degree of unsaturation, but the proportions of the various fatty acids are fairly uniform in fats and oils of common origin. Any fatty triglyceride can be used as a raw material for fatty alcohol manufacture. The most common starting materials, for which one or more manufacturers have developed processing conditions, are coconut oils, palm kernel oil, sperm oil, castor oil, menhaden and other fish oils, tallow, and lard (see Fats and fatty oils; Fatty acids).

A smaller amount of certain fatty alcohols is obtained commercially from naturally occurring esters of the alcohols (see p. 551).

Properties

Chemical Properties. Higher alcohols of fatty origin undergo the same chemical reactions as any primary monohydric alcohol (see Alcohols). The reactivity in most chemical reactions decreases with increasing molecular weight. The lower solubility of the higher alcohols in water and other solvents generally requires modification of processing conditions. The following reactions are typical of fatty alcohols.

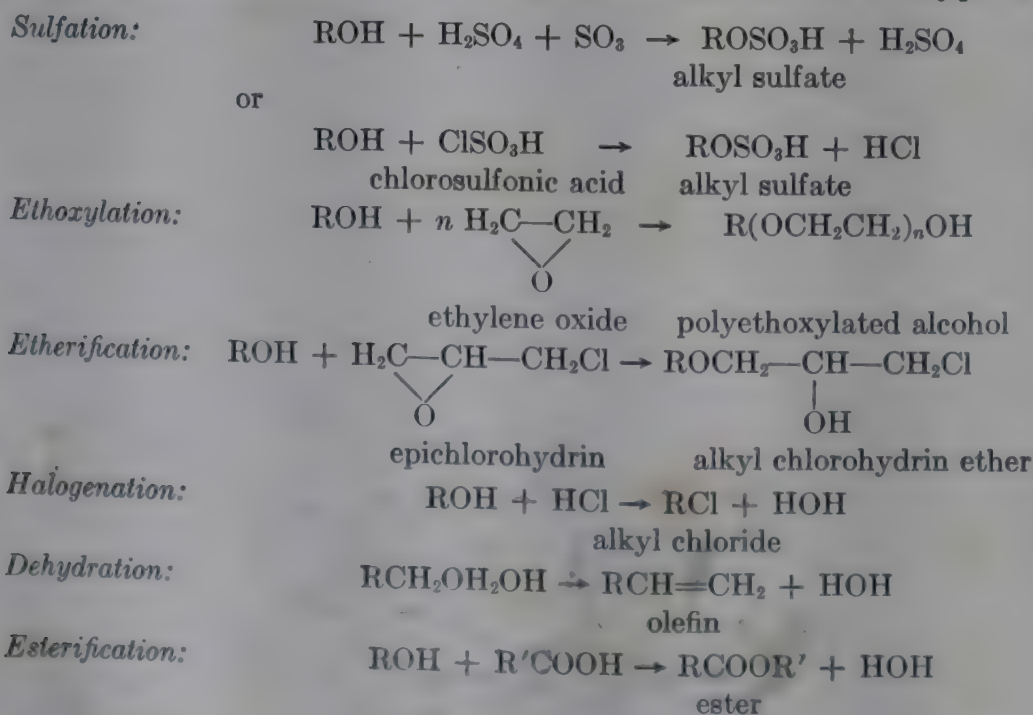


Table 1. Physical Properties of Pure Alcohols (Natural)

IUPAC name	Molecular formula	Other common names	Specific gravity, 20/20°C ^a	Refractive index, 20°C ^a	Bp, °C, 760 mm ^a	Mp, °C	Viscosity, cps ^a	Solubility, % by wt	
								in water	of water in other solvents
<i>Primary normal aliphatic</i>									
1-hexanol	C ₆ H ₁₄ O	n-hexyl alcohol	0.8191	1.4133	156	-44.6 ^b	5.9	0.59 ²⁰	7.2 petroleum ether, ethanol
1-heptanol	C ₇ H ₁₆ O	n-heptyl alcohol	0.8223	1.4233 ²²	176	-35	7.4	0.10 ¹⁸	
1-octanol	C ₈ H ₁₈ O	n-octyl alcohol	0.8254	1.4304	196	-16	8.4	0.06 ²⁵	4.5 ethanol, chlorine, petroleum ether
1-nonanol	C ₉ H ₂₀ O	n-nonyl alcohol	0.8284	1.4320 ²⁵	214	-5	11.7		
1-decanol	C ₁₀ H ₂₂ O	n-decyl alcohol	0.8310	1.4375	236	7	13.8		2.8 glacial acetic acid, benzene, ethanol, petroleum ether
1-undecanol	C ₁₁ H ₂₄ O	n-undecyl alcohol	0.8334, 23/4°C	1.4404	131 ¹⁵	19	17.2	<0.02	
1-dodecanol	C ₁₂ H ₂₆ O	n-dodecyl alcohol lauryl alcohol	0.8309, 24/4°C	1.4282 ⁶⁰	255-259	23	18.8	i	1.3 petroleum ether, ethanol
1-tridecanol	C ₁₃ H ₂₈ O	n-tridecyl alcohol	0.8223, 31/4°C	155 ¹⁵		30.6			
1-tetradecanol	C ₁₄ H ₃₀ O	n-tetradecyl alcohol myristyl alcohol	0.8236, 38/4°C	167 ¹⁵		38.3		<0.02	nil petroleum ether, ethanol
1-pentadecanol	C ₁₅ H ₃₂ O	n-pentadecyl alcohol				43.8			
1-hexadecanol	C ₁₆ H ₃₄ O	cetyl alcohol	0.8176, 50/4°C	1.4283 ^{78, 9}	189.5 ¹⁵	49.6	53 ⁷⁵	0.06 ²⁰	nil 102 ethanol, 97 methanol
1-heptadecanol	C ₁₇ H ₃₆ O	palmityl alcohol				53			
1-octadecanol	C ₁₈ H ₃₈ O	margaryl alcohol stearyl alcohol	0.8124, 59/4°C	1.4390 ⁶⁰	210.5	58		i	nil
1-nonadecanol	C ₁₉ H ₄₀ O	n-octadecyl alcohol				62			
1-duodecanol	C ₂₀ H ₄₂ O	n-nonadecyl alcohol eicosyl alcohol			220 ³	65-66		i	nil benzene, ethanol, petroleum ether
1-hexacosanol	C ₂₆ H ₅₄ O	arachidyl alcohol							
1-hentriacontanol	C ₃₁ H ₆₄ O	ceryl alcohol			305 ²⁰	79.5		i	
8-hexadecenyl-1-ol	C ₁₆ H ₃₂ O	melissyl alcohol myricyl alcohol	0.7770, 95/4°C			85.88			nil
9-octadecenyl-1-ol	C ₁₈ H ₃₆ O	palmitoleyl alcohol		205-210 ¹⁵					
10-eicosenyl-1-ol	C ₂₀ H ₄₀ O	oleyl alcohol	0.8489, 58/4°C	1.4473 ⁶⁰					
<i>Secondary normal aliphatic</i>									
2-octanol	C ₈ H ₁₈ O	eicosenyl alcohol capryl alcohol	0.835, 15/4°C	1.4256	178-179	-38	8.2	0.096 ²⁵	ethanol, petroleum ether

^a 20°C if not otherwise noted.^b As given in *Physical Properties, Synthetic Organic Chemicals*, Union Carbide Chemicals Corp., N.Y., 1962.

Physical Properties. The homologous series of primary alcohols exhibit definite trends in physical properties (see Table 1) (2-20). For every added CH_2 unit, the normal boiling point increases about 20°C and specific gravity (d_{20}^{20}) increases about 0.003 units. Increasing molecular weight decreases water solubility to nil above C_8 and increases solubility in oil. Below C_{12} , the fatty alcohols are colorless, mobile, oily liquids. 1-Dodecanol solidifies at slightly below room temperature, but the commercial product is generally fluid. Above C_{12} the physical form of the solid alcohols progresses from soft, crystalline platelets to crystalline waxes. The solubility of water in 1-hexanol is appreciable, but the water tolerance of the higher alcohols decreases rapidly with increasing molecular weight, and is negligible above dodecanol. The viscosity of the saturated normal primary alcohols as a function of temperature is shown in Figure 1; the liquid and vapor enthalpies for alcohols C_6 - C_{18} at various temperatures are shown in Figure 2.

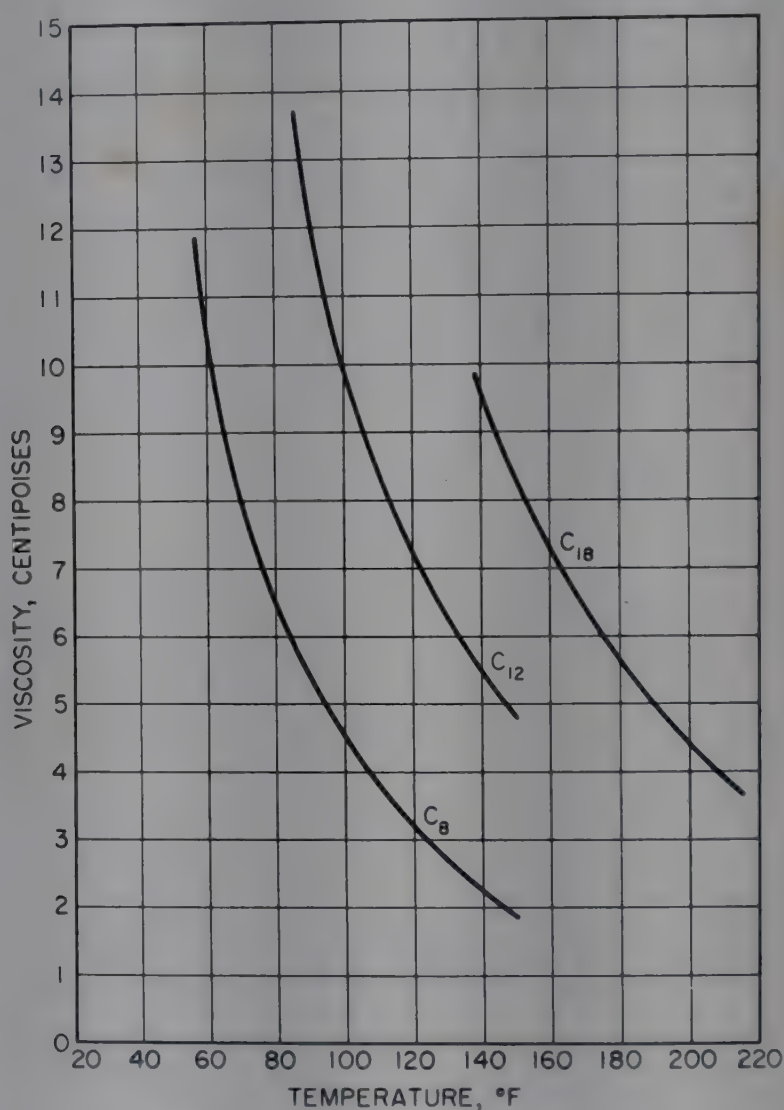


Fig. 1. Viscosity of fatty alcohols.

Manufacture by Reduction from Fatty Acids

Two reduction processes have attained major commercial importance.

1. Reduction of triglycerides or esters of the fatty acid by the use of metallic sodium and a reducing alcohol in the presence of a solvent.
2. High-pressure hydrogenolysis of triglycerides, fatty acids, or fatty acid esters in the presence of specific catalysts.

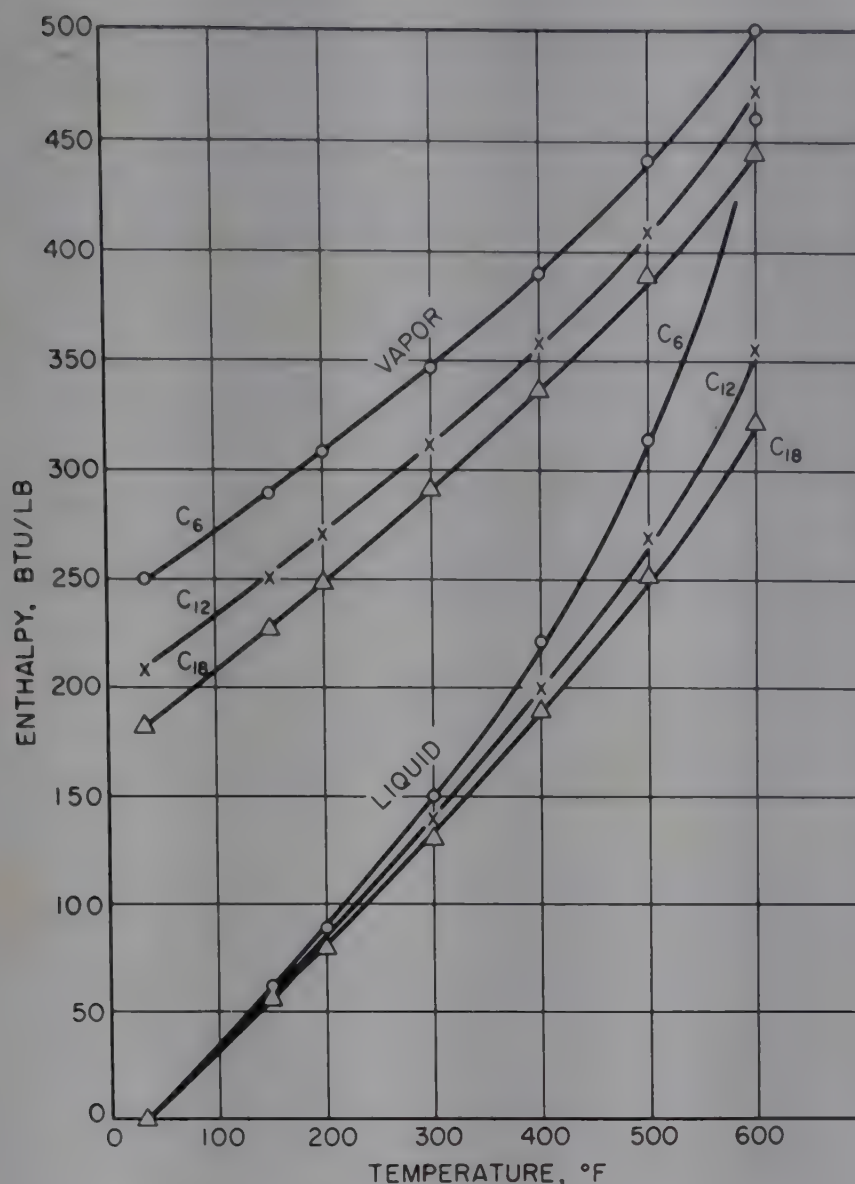
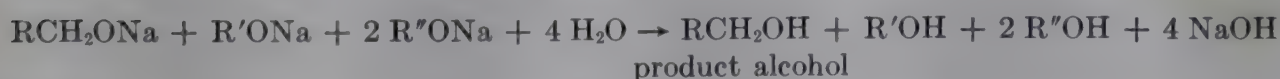
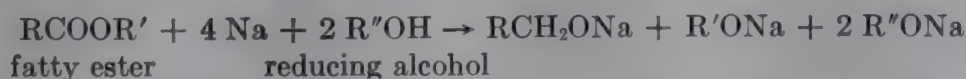


Fig. 2. Liquid and vapor enthalpies for alcohols C_6 – C_{18} at various temperatures. Plotted from computer data programmed according to the relationships proposed in the following: P_c and T_c by the method of Lydorsen (21a); C_p at 68°F by the method of Johnson and Huang (21b); Extrapolation of C_p to other temperatures by the method of Chow and Bright (21c); normal boiling points from Procter & Gamble data; latent heat at normal boiling points calculated from the simplified Clapeyron equation of Giacalone (21d); latent heat extrapolated to other temperatures by the same method of Watson (21e).

OUTLINE OF PROCESSES

Sodium Reduction. This may be considered as a variant of hydrogenolysis in which hydrogen is obtained from reaction of metallic sodium with a reducing alcohol.

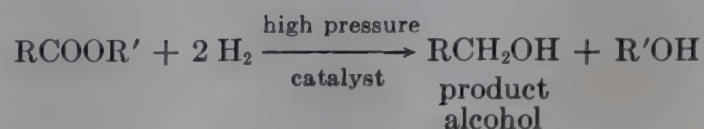


The original sodium reduction reaction (originated by Bouveault and Blanc in 1903 as a satisfactory laboratory technique) was relatively inefficient from the commercial production viewpoint. Experimental work conducted since 1930 by Hansley, Peddicord, and others has resulted in a process which provides excellent yields of alcohol of the highest purity available commercially. These studies have led to the use of cyclohexanol or 4-methyl-2-pentanol as the reducing alcohol and xylene or toluene as the solvent (secondary alcohols are the best reducing alcohols since primary

alcohols and sodium react directly with an evolution of hydrogen, and tertiary alcohols do not give complete reaction). The sodium reduction process can be applied to glycerides or to esters of the fatty acids with monohydric alcohols.

Ethylenic bonds in long alkyl chains are unaffected by the sodium reduction process. An exception is a pair of conjugated double bonds wherein the conjugation will be destroyed by a 1,4 addition which leads to a single double bond. For certain product application, retention of the ethylenic bonds is a particularly attractive feature of the sodium reduction process. If a saturated alcohol is the desired final product, the original triglyceride is normally hydrogenated prior to reduction (see Fats and fatty oils).

Hydrogenolysis. Hydrogenolysis was also investigated during the 1930s by a series of workers. The general conditions for catalytic hydrogenolysis of esters are 200–300 atm pressure and approximately 300°C. Above 330°C hydrocarbon formation increases noticeably.



Other by-products of hydrogenolysis are high-molecular-weight esters. Catalyst selection has a marked effect on hydrogenation of ethylenic bonds in the alkyl chain. With a nonselective copper chromite catalyst the final alcohol will be highly saturated. Hansley and others claim relatively little attack on the carbon double bond when a selective catalyst (cadmium–copper–zinc chromite) is used (22,23). A proposed commercial process employs specific fixed-bed catalysts in two different reactors (1). In the first reactor, the ester is reduced to alcohol and in the second, the ethylenic bonds are saturated. Reviews on these two processes have appeared in the literature (24–26).

RAW MATERIAL PREPARATION

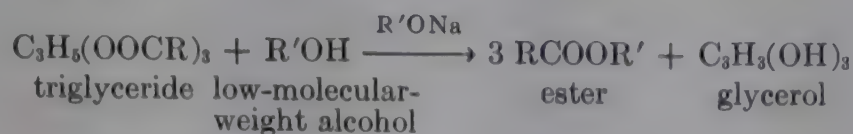
Pretreatment. The triglycerides are alkali refined (see Fats and fatty oils) and dried to minimize free fatty acid and water both of which are detrimental in the subsequent stages.

Although both the sodium reduction process and the high-pressure hydrogenolysis process can be carried out on the triglycerides, it is usually preferable to use esters of the fatty acids obtained from the triglycerides by alcoholysis. For the sodium reduction process this step eliminates the problem of glycerol recovery from caustic solution, and for the hydrogenolysis it eliminates loss of glycerol through decomposition and the consequent difficulties in separation of reaction products.

For the high-pressure hydrogenolysis it is also possible to use the free fatty acids, which are obtained from the triglycerides by conventional fat splitting (see Fatty acids). This variation is used in a number of installations. However, most of the recent installations employ hydrogenolysis of fatty acid esters.

Alcoholysis. For alcoholysis (ester interchange) prior to high-pressure hydrogenolysis, a low-molecular-weight alcohol, usually methanol, is normally employed. For alcoholysis prior to sodium reduction, an alcohol the same as the reducing alcohol is selected. When correct proportions of reducing alcohol and solvent for the sodium reduction process are used in the preliminary alcoholysis, the newly formed fatty acid ester does not have to be isolated. Sodium alcoholate, resulting from reaction of

metallic sodium with the selected alcohol, is employed as a catalyst for alcoholysis. The generalized equation is



The fatty acid esters are prepared, batchwise in a carbon-steel reactor, by treating the triglyceride with excess alcohol in presence of the catalyst for 15–30 minutes. The catalyst can be prepared in the same vessel (just prior to alcoholysis) by adding metallic sodium to the same alcohol. On settling, the reaction product, glycerol, separates as a lower layer. The ester layer is water-washed and dried. Approximately 80 weight percent of the theoretical glycerol yield is recovered by the settling operation. For both interesterification variations, the sodium usage is approximately 0.3–1.5 weight percent of the triglyceride employed.

REDUCTION PROCESSES

Sodium Reduction Process. The basic operation of the sodium reduction process is diagrammed in Figure 3. All steps of this process are conducted at atmospheric pressure in mild-steel reactors. The reaction is carried out by slurring metallic sodium in solvent and by adding ester, reducing alcohol, and solvent in correct proportions. An exothermic reaction, which is carried out at the boiling point of the mixture, occurs. The heat of reaction (2400 Btu/lb of sodium) is removed by refluxing solvent through an external cooling coil. Upon completion of the reaction the sodium alcoholates are “quenched” by dropping into another reactor containing water. Hydrolysis of the alcoholates causes formation of two phases—an upper organic layer (consisting of solvent, reducing alcohol, and fatty alcohol) and a lower caustic layer. The solvent and reducing alcohol are recovered by distillation for re-use. The remaining fatty alcohol is distilled from any residual bottoms and fractionated. The series of fatty alcohols, like their corresponding fatty acids, can be readily separated from each other by fractional distillation in bubble-cap columns under reduced pressures. However, like the fatty acids, the separation of saturated and unsaturated alcohols of equal chain length must be accomplished by other techniques, ie, fractional crystallization. The details of the sodium reduction process are presented by Kastens and Peddicord (24). The equipment, which theoretically could consist of only a few tanks and a reaction vessel, is complex in actual operation due to the additional items required for efficient recovery of the reactants and products and the elaborate precautions required in the use of metallic sodium.

High-Pressure Hydrogenolysis Process. The catalyst usually employed in the hydrogenolysis process is a complex mixture of cupric oxide and cupric chromite, in the form of a finely divided powder (27,28). The making of the catalyst consists of reacting copper nitrate and chromic oxide with ammonia, followed by vacuum filtration, water washing and, finally, roasting. The roasting operation must be closely controlled to provide a catalyst of uniform and high activity. Continuous roasting with very accurate temperature control gives the best catalyst. In the resultant complex mixture, copper oxide is considered the true catalyst, and the copper chromite, very stable at high temperatures, acts as a stabilizer of the copper oxide. The stability of this catalyst is excellent and is believed to be due to molecular dispersion of the copper oxide throughout the copper chromite.

For simple and economic operation of the process, it is essential to start with

into the bottom of the first reactor at a feed rate of approximately 5 weight percent of the ester. Hydrogen from the gas plant is compressed to operating pressure, heated to operating temperature, and introduced into the bottom of the first reactor through a distributing pipe. The reaction takes place as the materials rise in the successive reactors. Approximately 30 moles of hydrogen are fed per mole of ester. The hydrogen serves not only as the reducing agent but also as a principal source of heat and agitation. The outlet stream from the final reactor contains hydrogen, fatty alcohol, methanol, catalyst, and small amounts of ester. At the first separator the liquid portion, containing fatty alcohol and catalyst, flows out the bottom, and the vapor portion, hydrogen, methanol, and some fatty alcohol, rises overhead. The liquid underflow portion is depressurized. This crude alcohol is cleared of catalyst by filtration. A portion of the catalyst is discarded, and the remainder is returned to the catalyst feed tank for reuse. The vapors from the first separator are heat-exchanged against incoming hydrogen, cooled with water, and sent to the overheads separator. From this, hydrogen is sent to a recycle compressor to join the system, and the condensate, containing methanol and some fatty alcohol, rejoins the main crude alcohol stream. The combined crude alcohol is sent to a stripper where the methanol is removed at atmospheric pressure and recycled. The stripped alcohol is usually fractionated at reduced pressure to give alcohols of the desired purity. The actual fatty alcohol cuts commercially produced depend on market requirements.

The hydrogenolysis process is controlled mainly by changing the reaction temperature, feed rate, catalyst level, or fresh catalyst usage. Commercial operation is at the highest rate, lowest temperature, and lowest fresh catalyst usage, commensurate with yield and alcohol quality.

PROCESS PERFORMANCE AND COMPARISON

The comparative advantages of the two reduction processes can be summarized as follows: The sodium reduction process (a) produces both saturated and unsaturated alcohols; (b) has a lower capital investment; and (c) is a somewhat simpler operation than hydrogenolysis. Hydrogenolysis (a) operates at a lower production cost; and (b) can operate either on fatty acids or esters.

Table 2. Sodium Reduction Alcohols

Source	Yield, %	OH, %	Quality characteristics of alcohol		
			Saponification value	Acid value	Iodine value
tallow	92	6.5	3.0	0.1	54
sperm	90	6.7	2.8	0.5	88
menhaden	94	6.3	4.1	2.7	88 ^a
castor	90	10.6	6.9	0.8	
linseed	92	6.3	5.0	0.5	202

^a Klu-Benham.

Illustrative of yields and alcohol quality obtainable from commercial production of sodium reduction alcohols are the data in Table 2 (26). The results are for crude undistilled alcohols (washed free of soap and caustic) derived from reduction of the corresponding triglycerides.

At the present time, both processes can be considered to provide essentially equal

overall yields (90–95%) of high-purity alcohol from any specific triglyceride. Difference in hydrocarbon content accounts for the slightly higher alcohol purity obtainable by sodium reduction. However, careful control of high-pressure hydrogenolysis of fatty acid esters will minimize the hydrocarbon content of the finished alcohol. The present U.S. trend favoring high-pressure hydrogenolysis is occasioned by lower overall manufacturing costs and much greater demand for saturated alcohols. For large-scale plant production, sodium reduction manufacturing cost approximates 1.5 times that of high-pressure hydrogenolysis, in spite of the higher initial capital cost for a hydrogenolysis installation.

Manufacture from Naturally Occurring Esters

Sperm oil is at present the only commercial source, of any consequence, of fatty alcohols derived from naturally occurring esters. Most whale oil consists of triglycerides, but the oil from the sperm whale has a low triglyceride content, the remainder being wax esters (esters of higher alcohols with higher fatty acids). The composition is slightly different for the head oil and the blubber oil, as shown in the Table 3 (29).

Table 3. Composition of Sperm Oil

Oil	Wax esters	Triglycerides
head oil	74	26
blubber oil	66	34

The crude sperm oil is cooled by refrigeration; about 10% of a white crystalline wax settles out and may be separated by filtration. The wax is sold as *spermaceti* (see Waxes). It consists essentially of cetyl palmitate, $C_{15}H_{31}COOC_{16}H_{33}$.

The filtrate is commercial grade liquid sperm oil (see Fats and fatty oils). It consists of the triglycerides, together with the portion of the wax esters that was not solidified, and contains approximately 30 percent of cetyl, oleyl, and arachidyl alcohols in the form of their esters with fatty acids. These fatty acids vary markedly both as to degree of unsaturation and chain length, depending on whether the source is the head or the blubber of the sperm whale. Fatty acids in the ester portion of the head oil are either saturated or monounsaturated, and range from C_{12} to C_{22} with only minor amounts of C_{20} and C_{22} acids.

The alcohols can be obtained from these esters by saponification with caustic soda followed by distillation. The alcohol yield is about 30% of the original oil. Since soap results from reaction of the soda and the fatty acids, hot concentrated caustic solution is employed to minimize foaming, which would interfere with the distillation (see Soap). An interesting improvement is to carry out the saponification in trichloroethylene in complete absence of water, with anhydrous caustic soda (30). This is followed successively by atmospheric distillation of trichloroethylene and vacuum distillation of the alcohols, leaving soap as bottoms.

This method of alcohol production is now of relatively minor importance and is not practiced in the U.S. However, it is employed in Japan and in Europe, where these fatty acids have a higher value than in the U.S. The resultant alcohols are imported into the U.S. and compete with similar alcohols from tallow and coco triglycerides.

Analysis

Since fatty alcohols are derived from natural products by a variety of processes and are, therefore, subject to variability in composition, the analytical procedures for these materials are designed to yield three kinds of information; (a) the composition of the alcoholic portion with respect to chain length and unsaturation; (b) the purity of the material; and (c) the determination of the presence of minor impurities and contaminants that could interfere with subsequent uses.

The analytical scheme is similar to that used for fatty acids (31). Gas-liquid partition chromatograph techniques are currently used to determine, quantitatively, various chain length alcohols and hydrocarbons. Hydroxyl value, HV (milligrams of KOH equivalent to the hydroxyl content of 1 gram of fat), measures the —OH end group and reflects both the average molecular weight of the alcohol and the purity. Saponification value, SV (milligrams of KOH required to saponify 1 gram of fat), acid value, AV (milligrams of KOH required to neutralize the free fatty acids in 1 gram of fat), and ester value, EV (SV minus AV), are measures of the carboxylic acid impurities, present as the free acid or as alcohol ester. Iodine value, IV (grams of iodine absorbed by 100 grams of sample), is a measure of the unsaturation present in the alcohol. In view of the hygroscopic nature of the fatty alcohols, moisture determinations are usually required. Various color indexes have been used, but the APHA color is the most popular. Carbonyl oxygen determinations are sometimes run if aldehydic impurities are crucial in the use of the product.

Specifications and Standards

The pure fatty alcohols are rarely of commercial importance. The major portion of fatty alcohols consumed industrially consists of mixtures of alcohols, usually fractionated from the whole cut alcohol (2,32–35).

A great variety of fatty alcohol products are available commercially. Approximate compositions for the most common mixtures are shown in Table 4. By far the bulk of commercial fatty alcohols are essentially saturated alcohols derived from coconut oil and animal fats. Aside from oleyl alcohols, a major component of sperm oil, minor amounts of unsaturated alcohols are available as specialty products made by the more costly sodium reduction process. With the refinement of gas-liquid chromatography techniques for the analysis of fatty alcohol mixtures, small amounts of C₁₅ and C₁₇ fatty alcohols have been identified. These odd-chain-length alcohols constitute less than 2% of whole cut alcohols and usually are not identified separately. Typical specifications for some commercially available fatty alcohol mixtures are shown in Table 5.

Cetyl and stearyl alcohol mixtures are used extensively in the drug and cosmetic industry (see Uses) and are produced to USP and NF specifications. NF specifications for cetyl alcohol require: mp, 45–50°C; AV, 2.0 max; IV, 5.0 max; HV, 218–238; and boiling range, 90% min between 316–336°C. USP specifications for stearyl alcohol require: mp, 56–60°C; AV, 2.0 max; IV, 2.0 max; HV 200–220.

The liquid fatty alcohols are available in 350-pound drums, 55-gallon drums and 4000- to 8000-gallon tank trucks or tank cars. The solid fatty alcohols are delivered in 50-pound paper bags, 50-pound fiber drums, 125-pound fiber drums, tank trucks, and tank cars. The tank trucks and cars are usually equipped with internal coils for heating for alcohols above decyl. Rail or truck shipments are classified as inedible

Table 4. Approximate Composition of Commercial Fatty Alcohol Mixtures

Common names	Representative trade names	Derived from	Approximate composition (% by wt, 100% alcohol basis)							
			C ₆	C ₈	C ₁₀	C ₁₂	C ₁₄	C ₁₆	C ₁₈	C ₂₀
octyl alcohol	Lorol ^a 20, Dytol ^b M-83 CO-8 ^c	CNO	1	98	1					
decyl alcohol	Lorol 22, CO-10	CNO		2	98	trace				
octyl-decyl alcohol	Umbrex ^c	CNO	5	54	39	2				
lauryl alcohol	Dytol L-79, CO-12	CNO			2	96	2			
lauryl alcohol	Lorol 9, Dytol A-24	CNO			1	71	26	2		
lauryl alcohol	Dytol B-35 CO-1214	CNO			1	65	25	9		
myristyl alcohol	Dehydag	CNO				2	95	3		
myristyl-cetyl alcohol	CO-1418	CNO				4	44	24	28	
cetyl alcohol	Dehydag, Lorol 24 Dytol F-11	CNO-tallow sperm					1	97	2	
cetyl-stearyl alcohol	Dytol E-46, Dehydag TA-1618	CNO-tallow					3	64	33	
cetyl-oleyl alcohol	Dehydag	sperm						50	50 ^d	
stearyl alcohol	Lorol 28	CNO-tallow						5	95	

^a Registered trademark for Du Pont fatty alcohols.
^b Registered trademark for Rohm & Haas fatty alcohols.
^c Registered trademark for Procter & Gamble fatty alcohols.
^d Oleyl.

fatty alcohol, NOIBN, derived from vegetable oils or animal fats; express shipments as Oil, Coconut, Inedible, or Fat, Animal, Inedible.

Fatty alcohols are hygroscopic, and drying tubes are recommended for tanks where long storage periods are expected.

Although fatty alcohols are stable under normal conditions of storage, long exposure of hot alcohols to air will result in an increase of aldehydic carbonyl content. These carbonyl impurities may have a deleterious effect on the color stability and reactivity of the alcohol in subsequent chemical reactions, particularly where catalysts are used.

Economic Aspects

The U.S. production of higher alcohols above C₁₀, as cited in the 1959 U.S. Tariff Commission Report, is 267,000,000 pounds. Sales for the same year are given as 83,000,000 pounds at a price of 22¢/lb.

More than two-thirds of the higher alcohols above C₁₀ are consumed in the manufacture of surfactants. The economics of fatty-alcohol manufacture are tied closely to the pricing of the two most extensively used raw materials, coconut oil and tallow. As surfactant raw materials, the fatty alcohols compete directly with petroleum-derived products, such as alkylbenzene and nonylphenol. The only major U.S. source of coconut oil is importation from the Philippines and the Far East. Coconut oil prices have fluctuated widely in the past 10 years, and the generally high price of CNO-derived fatty alcohols has encouraged the use of the stable, low-priced petroleum

Table 5. Typical Specifications for Commercial Fatty Alcohols

Common name	Alcohol, % min	Hydro-carbon, % max	Hydroxyl value	Ester value, max	Acid value, max	Iodine value, max	Specific gravity, 25/25°C ^a	Melting point, °C	Boiling range, °C	Color, APHA	Moisture, % max
octyl	98	2	415-440	1.3	0.2	0.5	0.815-0.825		193-197	15	0.2
lauryl (96% C ₁₂)	98	2	285-300	2.0	0.4	0.5	0.827-0.832		253-257	50	0.1
lauryl (70-90 C ₁₂)	98	2	282-297	2.0	0.4	0.5	0.832-0.835	20-24	257-282	50	0.1
myristyl-cetyl	98	2	234-245	3.0	0.4	0.5	0.809	41	295-320	50	0.1
cetyl-stearyl (tallow alcohol)	96	4	208-223	3.0	0.3	1.0	0.809-0.816	50-54	316-332	100	0.1
cetyl	98		218-230	2.5	1.0	5.0	0.815-0.825 ⁵⁰	45-50	316-330	100	0.1
stearyl	96	4	190-210	2.0	1.0	3.0	0.810-0.815 ⁶⁰	55	343-363	100	0.1
cetyl-oleyl	98		215-230		1.0	40-45	0.84 ⁴⁰	31	310-340		

^a Except where otherwise noted.

chemicals. Alcohols derived from animal fats have had a relatively stable, low-cost source of raw material.

If the question of detergent removal in sewage treatment and in surface waters is solved by the use of biodegradable surfactants rather than by some other method, an increase in the market for fatty alcohols would be expected because fatty alcohol derived surfactants generally are rapidly and completely biodegradable.

Uses

Fatty alcohols and fatty alcohol derivatives are used in a bewildering variety of industrial and consumer products (36). Many of the applications for which fatty alcohols have been recommended are listed in Table 6. The more important individual applications are discussed at greater length below.

Table 6. Uses for Fatty Alcohols

Industry	Use
detergent	emollient, chemical intermediate, foam builder
petroleum	emulsifier, ^a lubricant, ^a dispersant, ^a antirust agent, ^a foamers ^a
agriculture	evaporation suppressant, pesticide ^a
chemical specialties	emulsifier, chemical intermediate, foam builder
plastics	plasticizer softener, ^a release agent, antifoamer, dispersant, antistatic agent, chemical intermediate
textile	lubricant, antifoamer, antistatic agent, chemical intermediate
cosmetics and pharmaceuticals	emulsifier, plasticizer softener, flavor and perfume component, ^a emollient, chemical intermediate, solvent
pulp and paper	plasticizer softener, antifoamer
food	emulsifier, ^a flavor component, ^a anti-antioxidant ^a
rubber	plasticizer softener, ^a dispersant
paint and protective coatings	emulsifier, ^a chemical intermediate
metalworking	lubricant
adhesives	plasticizer softener
ore processing	flotation agent, solvent, foamers ^a

^a A fatty alcohol derivative is used.

Surfactants. The surfactant derivatives of fatty alcohols find wide application in every industry where emulsifying, dispersing, wetting, or detergent properties are desired (see Detergents; Emulsifiers; and Wetting agents). Fatty alcohols are used as starting materials for all surfactant types, ie, anionic, nonionic, and cationic (37-39). Lauryl alcohol sulfate, C₁₂H₂₅OSO₃H (generally includes myristyl sulfate), is noted for its solubility and rapid voluminous foaming ability. The alkyl sulfates are used extensively in shampoos, specialty cleaning compounds, toothpastes, and light-duty detergents. Alcohol sulfates have been replaced by the newer sulfated polyethoxylated lauryl alcohols (C₁₂H₂₅(OCH₂CH₂)_nOSO₃H) in many applications.

Sulfated tallow alcohols (ROCO₃H, R = C₁₆H₃₃ and C₁₈H₃₇) are excellent textile detergents and have found wide acceptance as surfactants in heavy-duty laundry detergents for consumer and commercial use.

Anionic surfactants derived from fatty alcohols below C₁₂ are generally poor detergents and find little application in formulated detergent products. However, many

of these materials are excellent foaming, wetting, and dispersing agents and find use in specialty industrial applications.

There are also a great number of less important anionic derivatives of fatty alcohols which find wide variety of application in specialty surfactant uses.

The principal nonionic derivatives of fatty alcohols are the polyethoxylated alcohols, $R(OCH_2CH_2)_nOH$. Wide latitude in the hydrophilic-lipophilic balance (HLB) is possible by variation of the alcohol chain length and number of moles of ethylene oxide added (41). Specific uses for these materials are too numerous to mention but they find wide application where emulsifying, wetting, and dispersing ability are required. One reason for the increasing popularity of nonionic detergents is compatibility with other ionic species in solution, for example, the cationic quaternary bactericides and herbicides.

Cationic quaternary nitrogen surfactants of various types may be synthesized by the condensation of tertiary amines with long-chain alkyl halides. Primary straight-chain alkyl halides are normally obtained by hydrohalogenation of the corresponding fatty alcohol $ROH + HCl \rightarrow RCl + H_2O$. The quaternary derivatives are widely used in disinfectants, bactericides, fungicides, antistatic agents, and textile softeners.

Plasticizers. The second largest consumer of fatty alcohols is the plasticizer industry (40). Fatty alcohols are used almost exclusively as intermediates in the manufacture of plasticizers for polyvinyl chloride. This market is limited to hexyl, octyl, and decyl alcohols since the plasticizers derived from higher alcohols have poor compatibility and/or performance. Di-*n*-octyl-*n*-decyl phthalates are the most popular product and compete directly with phthalate esters derived from oxo alcohols. Hexyl, octyl, and decyl alcohol esters of dibasic acids (adipic, azelaic, sebacic) are also used in specialty plasticizer applications.

Cosmetics. Cetyl and stearyl alcohols are used extensively in the pharmaceutical and cosmetic industry as water/oil emulsifiers, creams, ointment, and suppository bases, emollient additives, and intermediates for perfume and flavor components (41-48). Use in the cosmetic industry was the first major commercial application of fatty alcohols, dating back to the early 19th century when cetyl alcohol was first isolated from spermaceti. The compatibility with cosmetic materials, mildness, skin feel, and nontoxicity of these saturated alcohols have maintained demand up to the present time. Toilet Goods Association, NF, and USP specifications for cetyl and stearyl alcohols are generally prerequisite for this application.

Lubricant Additives. A rapidly developing use for lauryl, myristyl, cetyl, and stearyl alcohols involves their use as chemical intermediates in the manufacture of polyacrylate viscosity index improvers. Fatty alcohols have been used for many years as gel stabilizers for metal soap-modified greases. Fatty alcohol esters of phosphorus acids are valuable additives to lubricating oils to maintain effective lubricating action under extreme pressures. Fatty alcohols also find applications as lubricants in metal drawing and other metalworking operations (49-53).

Evaporation Suppression. Many compounds containing hydrophobic and hydrophilic structural components will form monomolecular films on water surfaces. The higher fatty alcohols, especially cetyl and stearyl, form compressed monomolecular films with surface pressures in excess of 40 dynes/cm. These compressed fatty alcohol films are capable of suppressing the evaporation of water up to 70%, under laboratory conditions (54), without undue interference with the exchange of the oxygen and car-

bon dioxide essential to marine life (55). Many monomolecular film-forming chemicals have been screened as evaporation retardants (56). The combination of effective evaporation suppression, nontoxicity (57), and modest cost of cetyl and/or stearyl alcohols has led to intensive field experimentation on ponds and reservoirs in many countries throughout the world (58–65). Current consumption of fatty alcohols as evaporation suppressants is confined largely to experimental programs. Field tests have variously shown a reduction in evaporation from 10 to 60 percent, the most frequent suppression being of the order of 30 percent (66). Costs of saving water by this technique range from \$4/acre-foot to \$2/1000 gallons. Serious problems related to application methods, wind effects, and biodegradation of the film remain to be solved before widespread use of this technique is possible.

Miscellaneous Applications. The fatty alcohols have been found suitable for defoaming applications in the pulp and paper and food processing industries (67). Hexyl and octyl alcohols are used as flotation frothers for the beneficiation of bituminous coals (68) and other flotation applications. Some applications of the lower fatty alcohols as selective solvents in ore purification have been reported (69).

Gallate esters of lauryl alcohol are widely used as preservatives and antioxidants in the food industry (70). Derivatives of octyl and decyl alcohol have been reported to be useful antibacterial and antifungal compounds (71).

Decyl alcohol has been recommended as a softener in compounding specialty rubbers (72) and hexyl alcohols have been used as promoters in SBR rubber polymerization (73).

The fatty alcohols are used as starting materials in the synthesis of a variety of perfume and flavor components (74). Condensation products of C_{10} – C_{16} alcohols and phosphorus pentoxide are reported to be efficient antistatic agents.

Condensation products of phenol and stearyl alcohol are reported to be anti-corrosion additives to lubricating oils (76). Vinyl ethers of the higher fatty alcohols have been used as copolymers with vinyl acetate in the manufacture of protective surface coatings (77).

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ALCOHOLS, HIGHER, SYNTHETIC

The higher alcohols considered here are the commercially important saturated aliphatic alcohols containing from six to thirteen carbon atoms, with the exception of those derived from fats, which are discussed under Alcohols, higher, fatty. Many of these synthetic alcohols have more or less highly branched chains so that a number of isomers are possible. In the higher ranges the number of possible isomers reaches an astronomical figure. For example, the calculated number of possible octyl alcohols is 89; for C_{10} alcohols, 507; and for C_{20} alcohols, over 5 million. Only a very small fraction of these alcohols have ever been prepared and identified, and an even smaller number are of commercial importance.

The lower members of this series are usually oily liquids, the viscosity of which increases with molecular weight. The compounds of higher molecular weight (beginning about C_{12}) are waxlike solids.

The physical properties of these alcohols are very similar to those of their straight-chain primary isomers (see Alcohols, higher, fatty).

In the early days of the chemical industry, the higher alcohols were available only from natural sources. Now, however, synthetically produced higher alcohols predominate in commerce mainly because they are less expensive, higher in purity, and readily produced at a relatively steady price from abundantly available raw materials, particularly petroleum products.

Manufacture

There are several widely different methods for manufacturing synthetic higher alcohols.

1. By the oxo process. An olefin, which is usually available from petroleum in very large supply, is reacted with carbon monoxide and hydrogen under high pressure and in the presence of a catalyst. The olefin undergoes hydroformylation to a mixture of aldehydes.



The mixture of aldehydes is then reduced to a mixture of the corresponding alcohols. This process is discussed under Oxo process.

2. By any of the processes involving an aldol condensation. See Alcohols (p. 539), and the various specific alcohols described below.

3. From olefins via alkylaluminums (see below). 2-Octanol, prepared from sodium ricinoleate, is also described in this article.

SYNTHESIS FROM ALKYLALUMINUMS

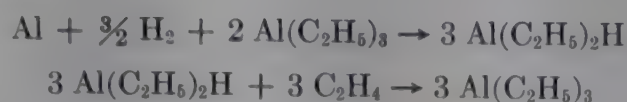
Methods for synthesizing alcohols from alkylaluminums were developed by Dr. Karl Ziegler at the Max-Planck-Institut für Kohlenforschung, Mülheim, Germany.

The Alfol process, based on the Ziegler patents (see Bibliography), is the basis of a plant constructed at Lake Charles, Louisiana, by Continental Oil Company, which is expected to come into production in 1962 with a capacity of 50,000 tons per year of alcohols. The alcohols are all straight-chain primary alcohols, with an even number of carbon atoms, ranging from C_2 to C_{20} .

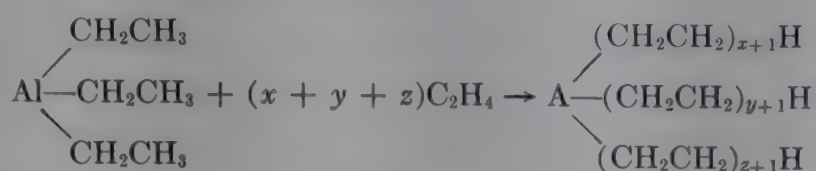
The following account is by courtesy of the Continental Oil Company, and is

based on a paper presented to the American Institute of Chemical Engineers in December 1961 by P. A. Lobo, D. C. Coldiron, L. N. Vernon, and A. T. Ashton.

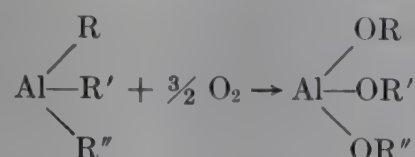
The first step is the preparation of triethylaluminum from aluminum, hydrogen, and ethylene. This is carried out in two stages, with recycle of two-thirds of the product, triethylaluminum.



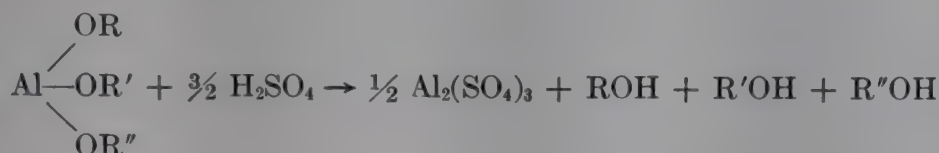
In the polymerization step ethylene is added.



The oxidation step converts this product to an aluminum alkoxide.



The alcohols are then formed by a hydrolysis step, which is carried out with sulfuric acid (strictly speaking, it is an acidolysis).



Preparation of Triethylaluminum (see also Aluminum compounds). High-purity aluminum is purchased as atomized powder. It is handled by a pneumatic conveying system, in which the oxygen content of the carrier gas is maintained at less than 2%. Hydrogen of approximately 90% purity is dried at 175 psig by an activated alumina drier. Other contaminants that might be deleterious are removed by scrubbing the gas at high pressure with a solution of triethylaluminum. The ethylene, from cavern storage, is extremely dry and has a high purity.

The aluminum powder is activated and then contacted with hydrogen and ethylene in the presence of a solvent to produce triethylaluminum in a two-step process. The reaction can be carried out in one step, although more effective utilization of raw materials can be obtained if two steps are used.

In the first step, active aluminum metal, hydrogen, makeup solvent, and recycle triethylaluminum are reacted under pressure to yield diethylaluminum hydride. This is contacted with ethylene under pressure in a second step to yield triethylaluminum.

Polymerization. Triethylaluminum is then reacted with ethylene at high pressure in a controlled polymerization reaction to produce higher molecular weight alkyls. The distribution of products of the polymerization follows a Poisson distribution and thus a spectrum of alkyls is obtained rather than a single molecular weight. A typical alkyl distribution is presented in Table 1. Operation to yield the distribution of Table 1 would result in the production predominantly of 1-hexanol, 1-octanol, and 1-decanol. If it is desired to maximize the manufacture of higher molecular weight alcohols, however, the polymerization conditions can be readily modified.

The polymerization reaction is highly exothermic, the heat of reaction closely ap-

Table 1. Typical Alkylaluminum Product Distribution

Alkyl	Weight percent	Alkyl	Weight percent
—C ₂ H ₅	1.14	—C ₁₄ H ₂₉	7.21
—C ₄ H ₉	9.56	—C ₁₆ H ₃₃	3.51
—C ₆ H ₁₃	17.42	—C ₁₈ H ₃₇	1.32
—C ₈ H ₁₇	24.46	—C ₂₀ H ₄₁	0.52
—C ₁₀ H ₂₁	20.90	—C ₂₂ H ₄₃	0.21
—C ₁₂ H ₂₅	13.75		

proximating that of the polymerization of ethylene. As water reacts violently with triethylaluminum, removal of this heat is accomplished by use of a double heat-exchange system. Isopentane is utilized as the intermediate heat-exchange fluid and the isopentane is cooled with water. This double heat-exchange system, although considerably more expensive than direct water cooling, eliminates the possibility of water leakage directly into the alkylaluminums.

Polymerization rate is increased by increases in both temperature and pressure. At temperatures much above 265°F, however, appreciable cracking of the alkyls takes place with the formation of olefins. Since this olefin formation increases the ethylene consumption of the process, operating temperatures of less than 265°F are favored. It has been found that at temperatures above 500°F and pressures much above 750 psig, the extremely rapid decomposition of ethylene in contact with triethylaluminum is possible. Consequently, it was absolutely necessary that high-speed scanning and automatic shutdown devices be installed on the polymerization reactor to insure that reaction conditions did not approach these limits.

Oxidation. Oxidation is carried out with air at above atmospheric pressure. The air is compressed and then dried to a dew point of —100°F before being introduced into the oxidation reactor. This removal of essentially all moisture from the air is necessary since water would hydrolyze the alkoxides to form alcohols. At this stage of the process, any alcohol formed results in a loss of product.

The oxidation step is also a highly exothermic reaction and heat removal considerations constituted a main factor in the oxidation reactor design. Water can be used for cooling at this stage in the process with safety since the higher alkylaluminums do not react as violently with water as does triethylaluminum.

The oxidation to aluminum alkoxides is not 100% selective and some by-products are formed: esters, ethers, acids, and aldehydes. It has been found possible, however, to minimize the formation of by-products by maintaining the reaction within a narrow band of operating conditions.

Alkoxide Purification. The oxidation by-products, process solvent, and the olefins formed during the growth reaction are removed from the alkoxides in a purification section.

Hydrolysis. Aluminum alkoxides can be hydrolyzed to alcohols with base, acid, or water to yield, respectively, the aluminate, acid salt, or aluminum hydroxide with the alcohols. At the Alfol plant the purified aluminum alkoxides are converted to alcohols by hydrolysis with sulfuric acid. A high-purity alum solution is formed as a coproduct of the reaction. It is possible, however, to produce a high-purity aluminum hydroxide with only a slight modification of the existing plant.

Concentrated sulfuric acid (98 wt %) is utilized. As it is desired to produce an

alum solution extremely low in iron content, only sulfuric acid of low iron concentration is purchased.

The alum is withdrawn from the reactor as a 27.8 weight percent solution to a rubber-lined storage tank. In storage the alum cools and any alcohols carried over with the salt solution settle out.

Neutralization. The alcohols are pumped from the hydrolysis reactor to a vessel where any residual sulfuric acid is neutralized with dilute caustic solution. The alcohols are then washed with hot water to remove the sodium sulfate formed during the neutralization step. Complete removal of this salt is necessary to prevent fouling of the reboilers during distillation of the alcohols.

Fractionation. The crude alcohols, containing a small amount of water, are dehydrated in the first few columns of the fractionation section. During this dehydration, 95% ethanol and pure 1-butanol are recovered as products. In the remainder of the fractionation columns, the alcohols are separated into individual fractions or two-component blends.

The fractionation columns have been designed to keep the residence time of the alcohols at a minimum temperature in order to insure high product quality. Towards this end, vacuum operation is utilized throughout a large portion of the distillation area. Liquid chromatographs have been installed on several of the columns and continuously monitor the overhead product.

Production. U.S. production of alcohols in the C₆–C₁₃ range was estimated at 255 million pounds in 1960. About 65% of this total went into plasticizers (qv) with the balance being consumed in detergents (see Detergency; Surfactants), synthetic lubricants, exports, and miscellaneous chemical derivatives. Minor derivatives include specialty solvents, pesticides, defoaming agents, flotation agents, perfumes, and pharmaceutical products. Table 2 lists physical properties, methods of production, producers, and tank car prices for the important synthetic higher alcohols of commerce.

Hexyl Alcohols

1-Hexanol (*n*-hexyl alcohol), CH₃(CH₂)₄CH₂OH; formula weight, 102.18. This alcohol is a colorless liquid with a mild odor. It is almost insoluble in water; it is soluble in ethyl alcohol and ether. It is found as an ester in the essential oil of the seed of *Heracleum giganteum*.

1-Hexanol can be made by reduction from ethyl caproate although this method of synthesis is of minor commercial importance. It may also be obtained as a by-product in the synthesis of *n*-butyraldehyde from acetaldehyde. 1-Hexanol is normally obtained from the process in yields of under 1% but conditions of the reaction can be modified so that the yield can be increased to approximately 10%. 1-Hexanol can also be synthesized via the trialkylaluminum process. This method of manufacture may eventually supplant the aldol process as the main source of the alcohol.

4-Methyl-2-pentanol, (CH₃)₂CHCH₂CH(OH)CH₃; formula weight, 102.18. This alcohol is a clear, colorless liquid with a moderately strong, penetrating odor. It possesses an asymmetric carbon atom, and two optical isomers have been isolated; the dextrorotatory form, prepared from the brucine salt of the acid phthalic ester, has $[\alpha]_D^{21.3} + 20.4^\circ\text{C}$, and the levorotatory form, obtained similarly from the brucine salt of the acid succinic ester, has $[\alpha]_D^{14} - 20.8^\circ\text{C}$. The commercial product is the racemic mixture.

Table 2. Synthetic Higher Alcohols

Number of carbon atoms	Name	Manu- facturing processes ^a	Melting point, °C	Boiling point, 760 mm	Specific gravity, 20/20°C	Solubility		Flash point, °F, open cup	Prices ^d			U.S. producers of synthetic alcohols, Jan. 1962 ^e
						% by wt, 20°C	in water		1952	1957	1962	
C ₅	1-hexanol	Al, Ta	-44.6	157.1	0.8205	0.58	7.2	165	33	33	27	3, 12
C ₆	4-methyl-2-pentanol	Al	-90 ^c	131.8	0.8083	1.7	5.8	106	13.5	14.5	14.5	10, 12
C ₆	2-ethyl-1-butanol	Al	-114.4	147.0	0.8343	0.43	4.6	128	28	28	31	12
C ₈	1-octanol	Ta ^b	-16	195	0.828			178	39.4	34.5	27	3, 4, 6, 9
C ₈	2-octanol	NS	+38.6	180	0.823				17.5	16.5	16.5	6, 7, 9
C ₈	2-ethyl-1-hexanol	Al	-70 ^c	184.8	0.8339	0.07	2.6	185	29	21.75	15	2, 11, 12
C ₈	isooctyl alcohol	Ox	-100 ^c	186.5	0.8323	0.07	3.5	185	26.5	21	15	1, 5, 8, 12
C ₉	mixed octyl alcohol	Al		179	0.831						18	11
C ₈	2,2,4-trimethyl-1-pentanol	Al	-70 ^c	168.3	0.8297	0.1	3.2	150			50	11, 12
C ₉	2,6-dimethyl-4-heptanol	Al	-65 ^c	178.1	0.8121	0.06	0.9	165			22	12
C ₁₀	1-decanol	Ta ^b	7	232	0.833				39.4	38.5	27.5	3, 4, 9
C ₁₀	"isodecanol"	Ox	-60 ^c	220	0.8395	<0.01	2.4	220		21	15	1, 5, 8, 12
C ₁₂	1-dodecanol	Ta ^b	24	257	0.835						37	3, 4, 9
C ₁₃	"tridecanol"	Ox	30.6	276	0.8357	<0.05	1.6	250		24	18	8, 12

^a Al, Aldol process; Ta, Trialkylaluminum process; NS, Natural sources; Ox, Oxo process.^b Also manufactured from fats.^c Sets to a glass at this temperature.^d Prices quoted are cents per pound in tank cars.^e

1. Amoco Chemicals Corp.

2. Celanese Chemical Co.

3. Continental Oil Co.

4. E. I. du Pont de Nemours & Co., Inc.

5. Gulf Oil Corp.

6. Harchem Div., Wallace & Tiernan, Inc.

7. Hatco Chemical Div., W. R. Grace & Co.

8. Humble Oil & Refining Co., marketed by Enjay Chemical Co.

9. Rohm & Haas Co.

10. Shell Chemical Co.

11. Texas Eastman Co., marketed by Eastman Chemical Products, Inc.

12. Union Carbide Chemicals Co.

4-Methyl-2-pentanol is made by reduction of the corresponding ketone, methyl isobutyl ketone (or its precursor, mesityl oxide, $(\text{CH}_3)_2\text{C}=\text{CHCOCH}_3$), which in turn is obtained by aldol-type condensation of 2 moles of acetone (qv). It is commercially produced in the United States by at least two producers and is readily available in tank car quantities.

This C_6 alcohol is a latent solvent in nitrocellulose lacquer formulations and is used to promote good flow characteristics and high gloss. It is also used as a moderate evaporating solvent in urea formaldehyde and alkyd-type surface coatings. 4-Methyl-2-pentanol finds use in ore flotation processes, either alone or as derivatives, and is an ingredient in some brake-fluid formulations.

2-Ethyl-1-butanol, $(\text{C}_2\text{H}_5)_2\text{CHCH}_2\text{OH}$; formula weight, 102.18. This hexyl alcohol is a colorless liquid with a characteristic odor and is miscible with most organic solvents. It is obtained commercially as a by-product from the aldol condensation of acetaldehyde to form *n*-butyraldehyde. It is available in limited tank car quantities.

2-Ethyl-1-butanol is used in the synthesis of surface-active agents, plasticizers, and lubricant additives. It also finds some use alone as a solvent in printing inks and surface coatings.

Heptyl Alcohols

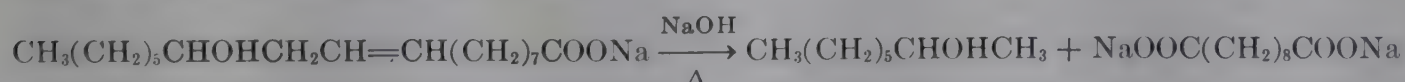
There are no commercially important heptyl (C_7) alcohols.

Octyl Alcohols

1-Octanol (*n*-octyl alcohol), $\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{OH}$; formula weight, 130.23. This alcohol is a colorless liquid with a penetrating, aromatic odor. It occurs in the form of esters in certain essential oils. It is obtained commercially as a by-product of the hydrogenation of coconut-oil fatty acids in the production of lauryl alcohol(1-dodecanol), stemming from caprylate (octanoate) esters present in the coconut oil. 1-Octanol produced by the trialkylaluminum process began to appear on the market in commercial quantities in 1962 at prices competitive with alcohol prepared from natural products. Highly refined grades of 1-octanol are used in perfumes and command a premium price (\$1.50–\$2.00 per pound). The technical grade is used in the manufacture of lubricating-oil additives and excellent plasticizers.

2-Octanol (capryl alcohol), $\text{CH}_3(\text{CH}_2)_5\text{CHOHCH}_3$; formula weight, 130.23. This alcohol is an oily, viscous, refractive liquid with an aromatic odor.

2-Octanol is made commercially by pyrolysis of sodium ricinoleate which in turn comes from the alkaline hydrolysis of castor oil. Sodium sebacate is obtained as a coproduct (see Acids, dicarboxylic).



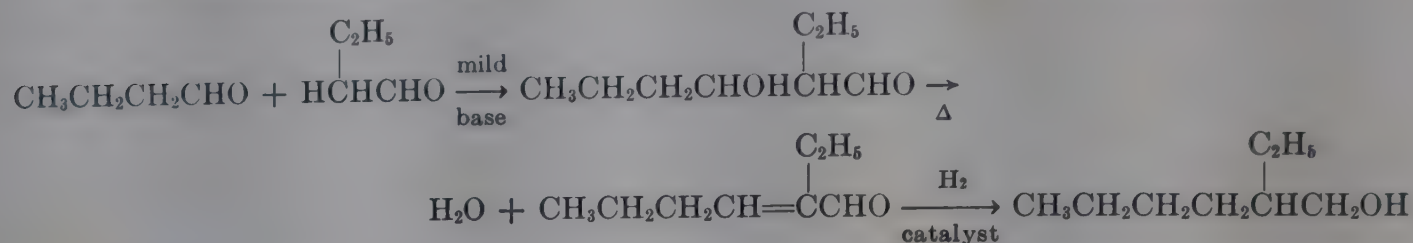
When commercially produced, this secondary alcohol contains about 15% of hexyl methyl ketone (2-octanone, $\text{CH}_3\text{COC}_6\text{H}_{13}$) as a by-product. The latter may be hydrogenated to 2-octanol. The purified grade of 2-octanol finds use in perfumes, in organic syntheses, and as an antifoaming agent. The technical grade is used as a solvent and also in the manufacture of dicapryl phthalate, a plasticizer.

2-Ethyl-1-hexanol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{OH}$; formula weight, 130.23. This alcohol is colorless and slightly viscous. With water it forms a heterogeneous,

constant-boiling mixture which boils at 99.1°C. The distillate, which contains 20% by weight of the alcohol, separates into two layers. The upper layer contains 97.4% of the alcohol and 2.6% water; the lower layer contains 0.10% of the alcohol and 99.9% water, all percentages by weight.

2-Ethyl-1-hexanol is the oldest, best known and most widely used of the synthetically produced higher aliphatic alcohols. Commercial synthesis began in the mid-1930s and by 1961 production had risen to an estimated 115 million pounds. It is predicted that output will rise to 210 million pounds by 1965. There are at present three commercial producers of 2-ethyl-1-hexanol in the United States.

2-Ethyl-1-hexanol is produced by the aldol condensation of *n*-butyraldehyde,



The *n*-butyraldehyde may be obtained by aldol condensation of acetaldehyde or by the oxo process from propylene.

The major use for 2-ethyl-1-hexanol is in the manufacture of plasticizers, principally di(2-ethylhexyl) phthalate or DOP. For the year 1961 an estimated 95 million pounds of 2-ethyl-1-hexanol went into production of plasticizers and synthetic lubricants. An additional 35 million pounds was exported, and the balance went into other derivatives such as esters, 2-ethylhexanoic acid, surfactants, antifoaming agents, and specialty solvents.

"Isooctyl alcohol." This commercial alcohol is not a pure chemical compound but a mixture of isomeric octyl alcohols. It is a clear, slightly oily liquid, essentially insoluble in water. Isooctyl alcohol is made via the oxo process from mixed heptylenes. A typical sample might have the following isomer distribution:

Isomer	Percent by weight
3,4-dimethyl-1-hexanol	20
3,5-dimethyl-1-hexanol	30
4,5-dimethyl-1-hexanol	30
3-methyl-1-heptanol	15
5-methyl-1-heptanol	
unidentified alcohols	5

Within the past decade isooctyl alcohol has become a chemical product of major commercial importance. Production in 1961 in the United States was estimated at 53 million pounds and is predicted to increase to 85 million pounds by 1965. Isooctyl alcohol and its derivatives resemble the corresponding 2-ethylhexyl compounds to a marked degree and the two are frequently used interchangeably. This alcohol is consumed almost exclusively in the manufacture of plasticizers. At the beginning of 1962, isooctyl alcohol was being produced in the United States by four companies. Three additional domestic companies have announced plans to enter production.

"Mixed octyl alcohols" is another commercial product which is not a pure chemical compound but a mixture of octyl alcohol isomers. It is available in

tank car quantities. Mixed octyl alcohol is a clear, oily liquid. It is manufactured by aldol condensation in a manner similar to that employed for 2-ethyl-1-hexanol except that in this case a major portion of isobutyraldehyde is included with *n*-butyraldehyde in the reaction. The resulting product is a 70–30 mixture of 2-ethyl-4-methyl-1-pentanol and 2-ethyl-1-hexanol. This commercial alcohol resembles 2-ethyl-1-hexanol even more closely than isooctyl alcohol and can be readily interchanged with the former. It is used to synthesize plasticizers and herbicides.

2,2,4-Trimethyl-1-pentanol $(\text{CH}_3)_2\text{CHCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{OH}$; formula weight, 130.23. This alcohol is an oily, colorless liquid with the pungent odor characteristic of most of the octyl alcohols. It is synthesized from isobutyraldehyde by a modified aldol process. This alcohol and its derivatives exhibit outstanding thermal stability. This property is attributed to the absence of hydrogen atoms on the beta carbon atom in the molecule. This alcohol is used in the manufacture of plasticizers, synthetic lubricants, and herbicides, and as a terminating agent for polyesters. The alcohol is presently offered by two United States chemical companies.

Nonyl Alcohols

2,6-Dimethyl-4-heptanol (sometimes referred to as diisobutylcarbinol), $(\text{CH}_3)_2\text{CHCH}_2\text{CHOHCH}_2\text{CH}(\text{CH}_3)_2$; formula weight, 144.26. This alcohol is prepared by the reduction of the corresponding ketone, diisobutyl ketone, which in turn is made by aldol-type condensation from three moles of acetone. 2,6-Dimethyl-4-heptanol is presently produced in the United States in limited commercial quantities. Principal uses of the alcohol are as a defoamer and as a reaction medium for the production of hydrogen peroxide.

Decyl Alcohols

1-Decanol (*n*-decyl alcohol), $\text{CH}_3(\text{CH}_2)_8\text{CH}_2\text{OH}$; formula weight, 150.28. This is a light yellow liquid with a sweet, fatlike odor. It is soluble in alcohol, ether, benzene, and glacial acetic acid, and insoluble in water.

Until very recently, 1-decanol was available commercially only by the catalytic reduction of coconut oil or coconut-oil fatty acids or esters under high pressure. However, the alcohol is expected to be commercially available in 1962 from the new trialkylaluminum process. This process yields a mixture of straight-chain alcohols with an even number of carbon atoms. While it is possible to fractionate and obtain 1-decanol of relatively high purity, the requirements of the consumer usually make it more attractive economically to offer a product which only contains a major proportion of 1-decanol. A typical commercial product may contain 55% 1-decanol and 43% 1-octanol. Major uses for this alcohol are in the manufacture of surfactants by sulfation or plasticizers by esterification. The alcohol itself finds some use as an antifoaming agent, and highly purified grades are used in perfume blends.

"Isodecanol." This inaccurate term is at present used for a commercial mixture of isomeric C_{10} alcohols. The alcohol is produced in large commercial quantities by the oxo process with a mixed stream of nonylenes as the charge stock. The major source of the nonylenes is polymerization of propylene, thus the charge stock is sometimes referred to as "tripropylene." The commercial product contains predominantly the isomeric trimethylheptanols; there are no compounds with a qua-

ternary carbon atom. Estimated production of isodecyl alcohol in 1961 in the United States was 55 million pounds and is predicted to rise to 75 million pounds by 1965. There are presently four commercial producers of isodecyl alcohol in the United States. Plasticizers are the major outlet, but isodecyl alcohol also finds use in synthetic lubricants, in the refining of uranium (as an ester of pyrophosphoric acid), as a specialty solvent, and as a defoaming agent.

Undecyl Alcohols

There are no commercially important undecyl (C_{11}) alcohols.

Dodecyl Alcohols

1-Dodecanol (*n*-dodecyl alcohol, lauryl alcohol), $CH_3(CH_2)_{10}CH_2OH$; formula weight, 186.33. This alcohol is a low-melting solid which is soluble in ether and ethyl alcohol but insoluble in water.

Lauryl alcohol has long been commercially available from the reduction of ethyl laurate prepared from coconut oil.

Lauryl alcohol may also be manufactured by the trialkylaluminum process, but again it is not advantageous to separate purified fractions. Two commercial grades of lauryl alcohol are offered from this process. One contains 55% lauryl alcohol and 43% myristyl alcohol (C_{14}). The other grade contains 60% lauryl alcohol, 25% myristyl alcohol, and 11% cetyl alcohol (C_{16}).

When converted to its sodium sulfate derivative ($-OH \rightarrow -OSO_3Na$), lauryl alcohol forms an important detergent with many properties superior to those of soap. This detergent can be used in soft and hard water and in slightly acid solutions that would precipitate the fatty acids from ordinary soaps. Pure sodium lauryl sulfate is not so useful a detergent as is a mixture with its higher homologs. Therefore, it is economically more advantageous to market the mixture than to separate the pure alcohol. Lauryl alcohol is used in the synthesis of mercaptans, which are used in rubber processing and for the synthesis of further derivatives.

Tridecyl Alcohol

A mixed tridecyl alcohol, often incorrectly referred to as "tridecanol," is made by the oxo process in a manner similar to that described for isodecyl alcohol. In this case the feedstock is a mixture of dodecylenes, usually obtained by a mild polymerization of propylene. An olefin fraction known as tetrapropylene is isolated to serve as the raw material. The major portion of this tridecyl alcohol is a mixture of isomeric tetramethylnonanols. An estimated 5 million pounds of tridecanol was produced in the United States in 1960, and this figure should double by 1965. There are presently two domestic producers.

Because of the high molecular weight of the tridecyl esters, they exhibit only limited compatibility with polyvinyl chloride, and hence this alcohol does not currently find a large outlet in the plasticizer field. Most of the tridecyl alcohol presently produced is used in the manufacture of anionic and nonionic synthetic detergents.

Tridecyl alcohol is used in synthesis of mercaptans, which are important in the processing of synthetic rubber and in the formation of other derivatives.

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Eastman Chemical Products, Inc.

ALCOHOLS, POLYHYDRIC

The term "polyhydric alcohols" refers to alcohols with three or more hydroxyl groups. The simplest and most important trihydric alcohol, glycerol, $\text{CH}_2\text{OHCHOHCH}_2\text{OH}$, is discussed separately (see Glycerol).

The term "sugar alcohols" is often used to denote a group of polyhydric alcohols obtained by reduction of carbohydrates. These sugar alcohols differ greatly from the remaining polyhydric alcohols of commerce and are therefore discussed in a separate section of this article.

Sugar alcohols.....	569
Bibliography.....	586
Other polyhydric alcohols.....	588
Bibliography.....	596

SUGAR ALCOHOLS

The sugar alcohols bear a close relationship to the simple sugars from which their names are derived (see Carbohydrates). The polyols to be discussed here contain straight carbon chains, each carbon atom bearing a hydroxyl group. Most of the sugar alcohols have the general formula, $\text{HOCH}_2(\text{CHOH})_n\text{CH}_2\text{OH}$, where n has values from 2 to 5. They are classified according to the number of hydroxyl groups as tetrityls, pentityls, hexityls, heptityls, etc. Each class contains stereoisomers. Counting meso and optically active forms, there are possible three tetrityls, four pentityls, and ten hexityls, all of which are known either from natural occurrence or through synthesis. Of the straight-chain polyols, sorbitol and mannitol have achieved the greatest industrial significance.

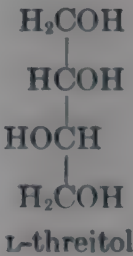
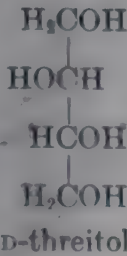
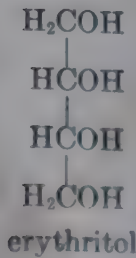
In general, these polyols are water-soluble, crystalline compounds with small optical rotations in water and have a slightly sweet to very sweet taste. Physical properties of the sugar alcohols discussed are listed in Table 1.

Table 1. Physical Properties of the Sugar Alcohols

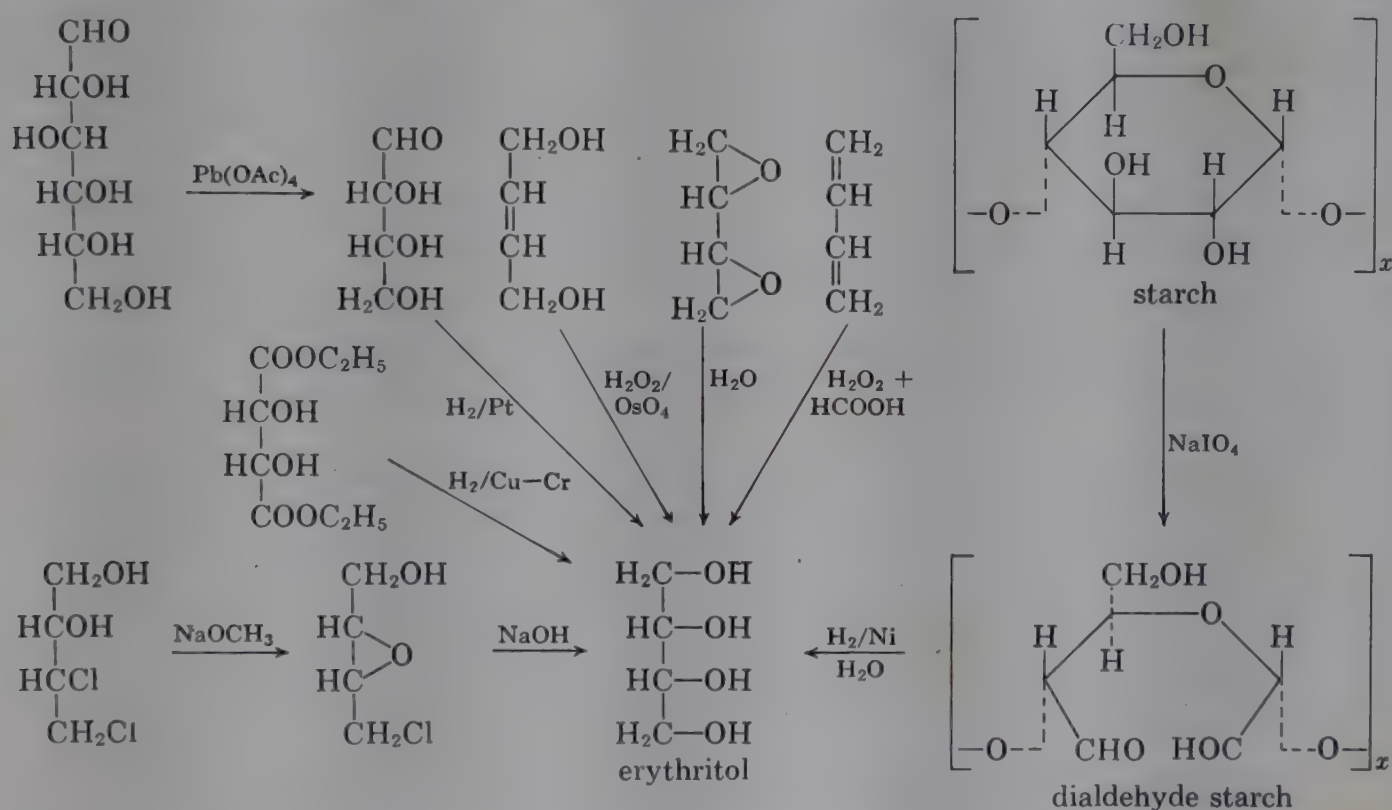
Sugar alcohol	Melting point, °C	Optical activity in H ₂ O, [α] _D ²⁰⁻²⁵	Solubility, g/100 g H ₂ O ^e	Heat of combustion, constant volume, kcal/mole
tetritols				
erythritol	120	meso	61.5	499.9 (94)
D-threitol	88.5-90	+4.3	very soluble	
L-threitol	88.5-90	-4.3		
D,L-threitol	69-70			
pentitols				
ribitol	102	meso	very soluble	
xylitol	61-61.5 (meta-stable) 93-94.5 (stable)	meso	179	
D-arabitol	103	+131 ^a	very soluble	
L-arabitol	102-103	-130 ^a		611.7 (124)
hexitols				
allitol	155	meso	very soluble	
dulcitol	189	meso	3.2 (15° C)	720.3 (94)
sorbitol (D-glucitol)	90.4-91.8 (meta-stable) 96.7-97.7 (stable)	-1.98	235	723.5 (6)
L-glucitol	89-91	+1.7		
D,L-glucitol	135-137			
D-mannitol	166	-0.2	21.3	722.1 (6)
L-mannitol	162-163			
D,L-mannitol	168			
D-talitol	88-89	+3.2	very soluble	
L-talitol	87-88	-2.9		
D,L-talitol	95-96			
D-iditol	73.5	+3.5		
L-iditol	75.7-76.7	-3.5		
heptitols				
glycero-gulo-heptitol	129	meso	very soluble	
D-glycero-D-ido-heptitol	129	+0.7	very soluble	
perseitol	187	-1.1	7.4 (18° C)	835.8 (124)
volemitol	153	+2.15	22.2 (14° C)	
octitol				
D-erythro-D-galacto-octitol	169-170	-11 ^b		

^a In aqueous molybdic acid (46).
^b In 5% aqueous ammonium molybdate (27).
^c At 25°C unless otherwise indicated.

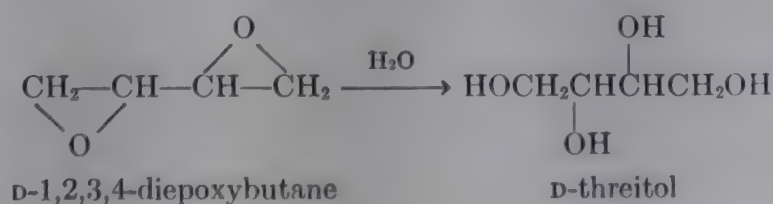
Tetritols

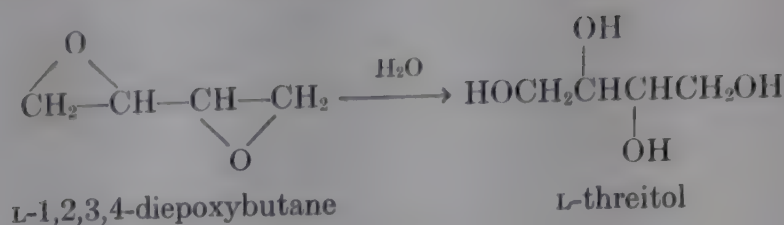


Erythritol occurs in lichens, algae, and yeasts. It can be obtained microbiologically from sugars by means of various species of fungi (20) including *Aspergillus niger* (147), by yeasts of the *Zygosaccharomyces* class (59), and by various osmophilic yeasts (106,120). It has been found in the urine of fasting men (130). A chemical conversion of glucose to erythritol consists of lead tetraacetate oxidation of glucose to an erythrose derivative, followed by reduction (95). Erythritol has been synthesized from *meso*-tartaric acid or its esters by catalytic reduction (131), or by reduction with lithium aluminum hydride (35). Hydration of *meso*-diepoxybutane results in erythritol (55,101). Hydroxylation of butadiene with hydrogen peroxide and formic acid leads to erythritol, along with D,L-threitol (64,65). A closely related reaction is the formation of erythritol from 2-butene-1,4-diol by the action of hydrogen peroxide in the presence of osmium tetroxide (103). Alkaline hydrolysis of 4-chloro-2,3-epoxy-1-butanol leads to erythritol (62). Erythritol is potentially available in large quantity, together with ethylene glycol, from the combined hydrogenation and hydrolysis of dialdehyde starch (114). Yields of over 70% erythritol have been described. Erythritol is one of the products obtained from reduction of the carbohydrate mixture obtained from the polymerization of formaldehyde (84). Hydrogenolysis of sorbitol leads to erythritol as well as other products (28).

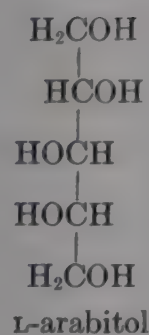
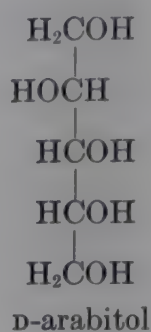
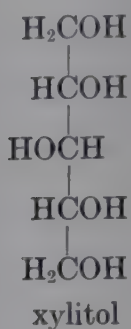


D- and L-Threitol have not been found in nature. The action of the wood-rotting fungus, *Armillaria mellea*, on glucose leads to D-threitol (17). The two enantiomorphs are synthesized by the reduction of D- and L-threose, respectively (66,83). Reduction of L-erythrulose leads to L-threitol as well as erythritol (15). L-Threitol is synthesized by the lithium aluminum hydride reduction of L-diacetyltartaric anhydride (92) or L-dibutyl tartrate (24,75). Of theoretical interest are the conversions of the D- and L-1,2,3,4-diepoxybutanes to D- and L-threitols, respectively (38).





Pentitols



Ribitol (adonitol) occurs in nature in the leaves of *Adonis vernalis*, in the roots of *Umbelliferae*, and in several Australian coccids. It is found in a combined form in riboflavin and as a constituent of the cell wall of several Gram-positive bacteria. Ribitol has been obtained by the catalytic hydrogenation of D-ribose (44) or by the reduction of L-ribose with sodium amalgam (41). It may be synthesized, along with D,L-arabitol, from noncarbohydrate sources by starting with a five-carbon acetylenic triol (102). Although D-ribose occurs naturally in nucleosides, it is not sufficiently abundant to make ribitol an inexpensive polyol.

Xylitol has not been found in nature. It is synthesized by reduction of D-xylose catalytically (73), electrolytically (29), and by means of sodium amalgam (42). Although D-xylose (wood sugar) is very widespread in nature, its recovery has not yet been effected economically. Thus xylitol is not a commercially available polyol. Xylitol also has been obtained by sodium borohydride reduction of D-xylonic acid γ -lactone (48).

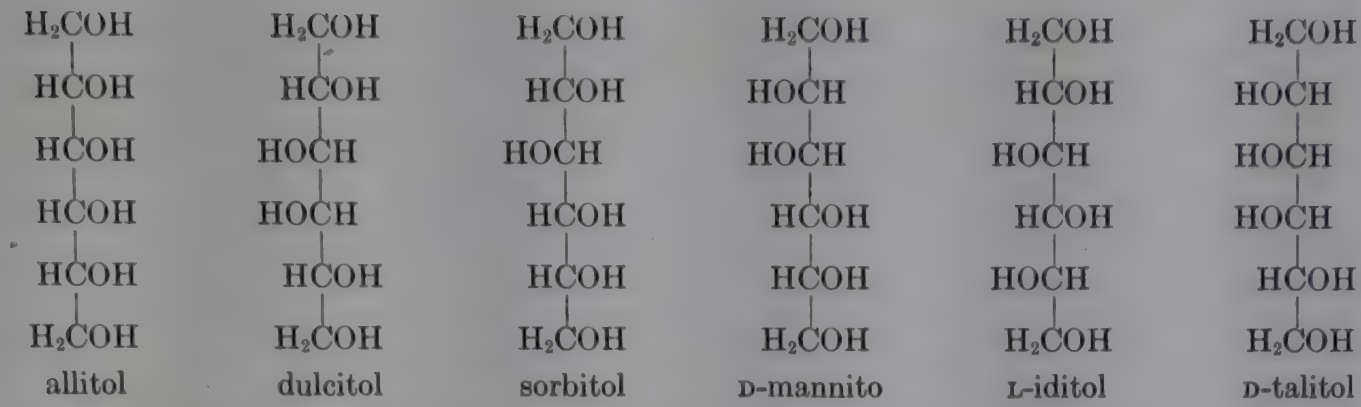
D-*Arabitol* is found in lichens and mosses and in combination in the uredospores of wheat stem rust (100). Fermentation of glucose by osmophilic yeasts produces D-arabitol in yields as high as 31% (106,118,119). In a study using ^{14}C labeled glucose it was found that C-1 of glucose was converted by the yeast to C-1 and C-5 in D-arabitol, while C-2 of glucose appeared in C-1, C-2, and C-4 of D-arabitol (117). The γ -lactones of D-arabonic and D-lyxonic acids are reduced by sodium borohydride to D-arabitol (48,142).

L-*Arabitol* has been found in urine of individuals having pentosuria (129). L-Arabitol may be synthesized by the reduction of L-arabinose which is abundant in nature. This reduction may be carried out both by chemical means (1) and by catalytic hydrogenation (56).

D,L-*Arabitol* has been prepared by the action of hydrogen peroxide in the presence of formic acid on divinyl carbinol (138). Another synthesis of D,L-arabitol, as well as ribitol, is from D,L-*erythro*-4-pentyne-1,2,3-triol, $\text{HOCH}_2\text{CHOHCHOHC}\equiv\text{CH}$ (102).

Hexitols

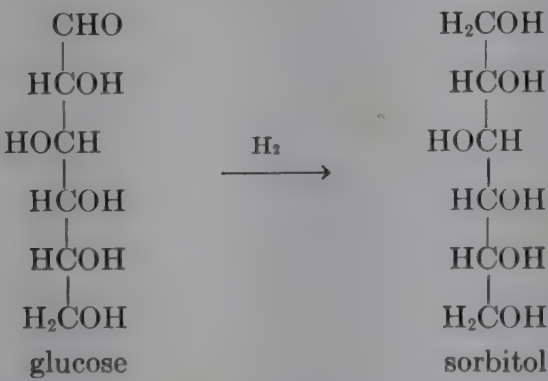
Allitol has been isolated from the leaves and branches of shrubs of the genus *Itea* (98). It has been synthesized by the catalytic hydrogenation of D-allose (122). Allitol also has been obtained from noncarbohydrate sources by oxidation of *meso*-1,5-hexadiene-3,4-diol ($\text{CH}_2=\text{CHCHOHCHOHCH}=\text{CH}_2$) with silver chlorate and osmium tetroxide which effects cis addition of hydroxyl groups (137). Similarly, oxi-



duction of *cis*-3-hexene-1,2,5,6-tetrol (HOCH₂CHOHCH=CHCHOHCH₂OH) results in the formation of both allitol and dulcitol (80).

Dulcitol (galactitol) occurs in a wide range of plants. It is found in certain yeasts, in shrubs of the *Euonymus* family (9,104), as well as in the mannas from a wide variety of plants. D-Galactose is reduced to dulcitol catalytically (73), electrolytically, (30) and chemically (16). Reduction of hydrolyzed lactose leads to both dulcitol and sorbitol. The dulcitol component, being relatively insoluble, is isolated by crystallization from the aqueous reduction mixture. Dulcitol is formed together with D-galactonic acid by treatment of D-galactose with alkali in the presence of Raney nickel (32). Reduction of D-galactonic acid γ -lactone with sodium borohydride leads to dulcitol (48, 144). Oxidation of a mixture of meso and racemic 1,5-hexadiene-3,4-diol with hydrogen peroxide and formic acid (trans addition of hydroxyl) leads predominantly to dulcitol, with some D,L-iditol (138,139).

Sorbitol (D-glucitol) was discovered initially in the fresh juice of mountain ash berries in 1872. It is found in fruits, such as apples, plums, pears, cherries, dates, peaches, apricots, and various berries, in algae, and in red seaweed. Since it occurs only to a very small extent in grapes, assay of the sorbitol content of wine has been used to detect its adulteration with other fruit wines or apple cider. Sorbitol is synthesized commercially by high-pressure hydrogenation of glucose as described in the section on manufacture below. Electrolytic reduction of glucose was formerly used for the manufacture of sorbitol (30). Chemical reduction of glucose to sorbitol has been effected by means of sodium amalgam and by reduction with cyclohexanol or tetrahydrofurfuryl alcohol in the presence of Raney nickel (2,3). Reduction of D-fructose leads to both sorbitol and mannitol. Hydrolysis and hydrogenation of sucrose or hydrogenation of invert sugar also results in the formation of sorbitol and mannitol (89). Both dulcitol

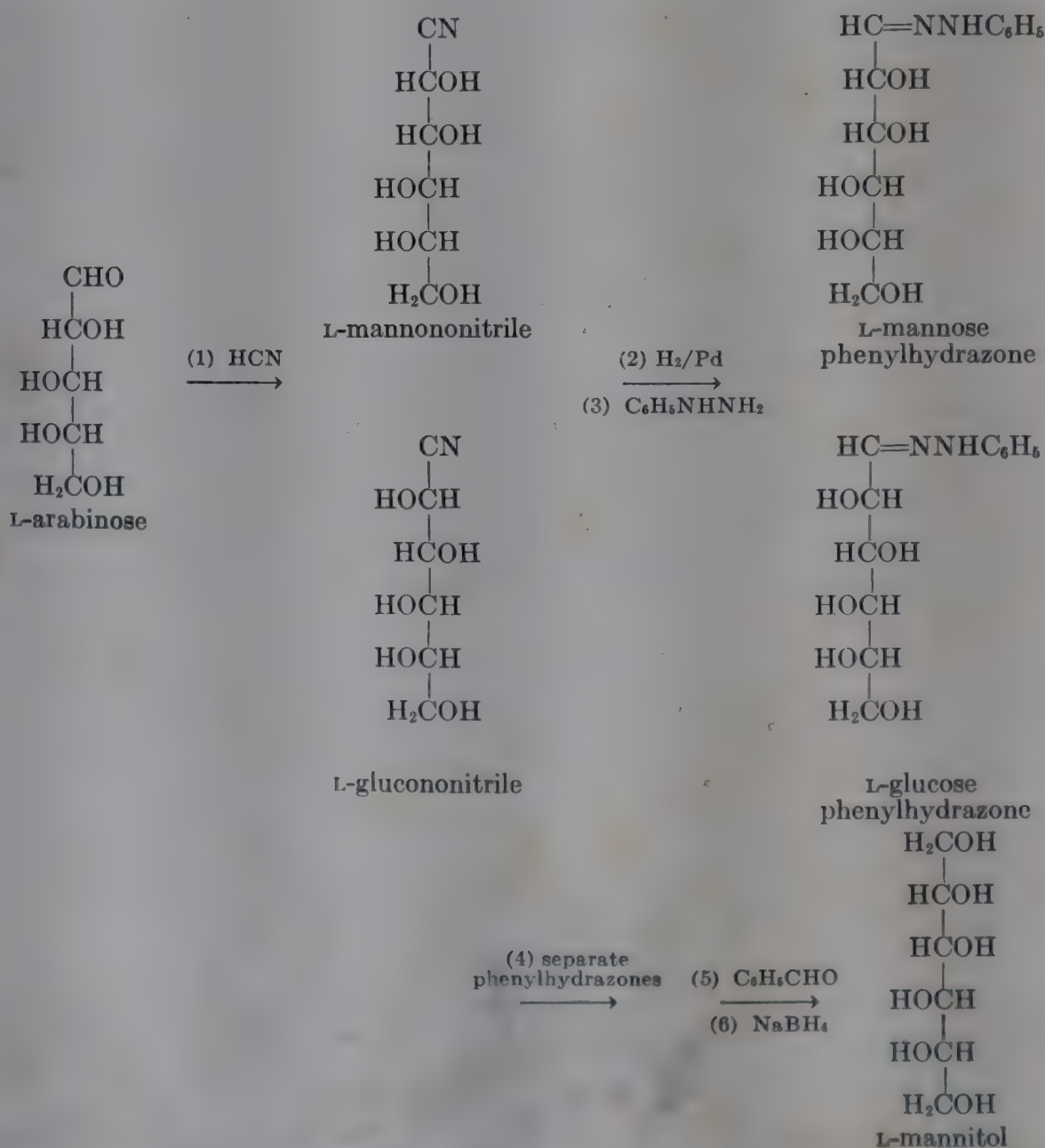


and sorbitol are obtained from the hydrogenation of hydrolyzed lactose. Reduction of partially hydrolyzed lactose, in addition, leads to lactitol (70). Sorbitol may be obtained by simultaneous hydrolysis and hydrogenation of starch (76). Both the γ - and δ -lactones of D-gluconic acid may be reduced to sorbitol (48).

L-Glucitol, which does not occur in nature, has been synthesized by reduction of D-gulose, D-sorbose, or D-gulonic acid γ -lactone (48).

D-Mannitol is widespread in nature. It is found to a major extent in the exudates of trees and shrubs such as the plane tree (80–90%), manna ash (30–50%), and olive tree. The manna ash, *Fraxinus rotundifolia*, formerly was cultivated in Sicily for the mannitol content of its sap. Mannitol occurs in the fruit, leaves, and other parts of various plants. This hexitol is present in pumpkin, mushrooms, onions, grasses, mistletoe, and lichens. It is found in the mycelia of various fungi. Mannitol occurs in marine algae, especially brown seaweed, with a seasonal variation in mannitol content which can reach over 20% in the summer and autumn (18). Microbial formation of D-mannitol, starting with fructose, glucose, or sucrose occurs with both fungi and bacteria (45). Fermentation of the tubers of Jerusalem artichokes leads to mannitol (107). Using sodium acetate as the sole carbon source, *Aspergillus niger* forms D-mannitol as well as D-arabitol, erythritol, and glycerol (11).

Although it cannot now compete commercially with other procedures, hydrolysis of mannan from vegetable ivory nut liberates pure D-mannose, which on catalytic, chemical, or electrolytic reduction produces D-mannitol in good yield. Reduction of fructose leads to both sorbitol and D-mannitol. Sucrose, on reduction under hydrolyzing conditions, also yields the same products in the ratio of three parts of sorbitol to one of D-mannitol. Commercially, D-mannitol is obtained by the reduction of invert sugar



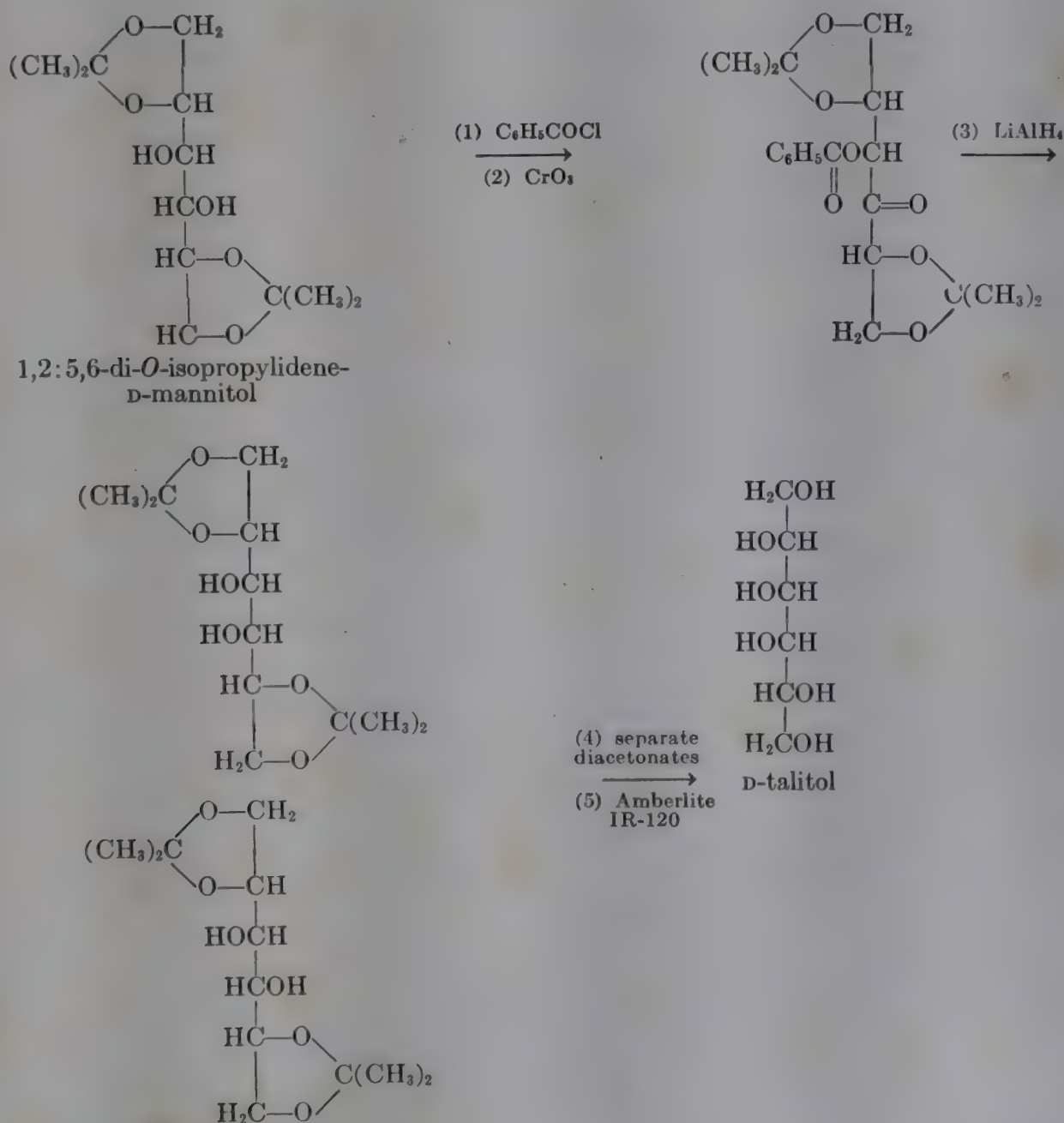
as described in the section on manufacture below. Hydrogenation or electrolytic reduction of aqueous alkaline solutions of glucose also leads to D-mannitol as well as sorbitol; indeed, over 20% of glucose can be converted to D-mannitol in this way. This is possible because of the interconversion of mannose, fructose, and glucose in alkaline media (*Lobry de Bruyn-Alberta van Ekenstein rearrangement*). Both the γ - and δ -lactones of D-mannonic acid are reduced catalytically to D-mannitol (50).

L-Mannitol does not occur naturally, but is obtained by the reduction of L-mannose or L-mannonic acid lactone (7). Synthesis of L-mannitol from the relatively abundant L-arabinose is achieved by the route shown on page 574, through its cyanohydrin (77).

D,L-Mannitol has been obtained by sodium amalgam reduction of D,L-mannose. The identical hexitol is formed from the formaldehyde polymer, acrose, by conversion through its osazone and osone to D,L-fructose (α -acrose) followed by reduction (40).

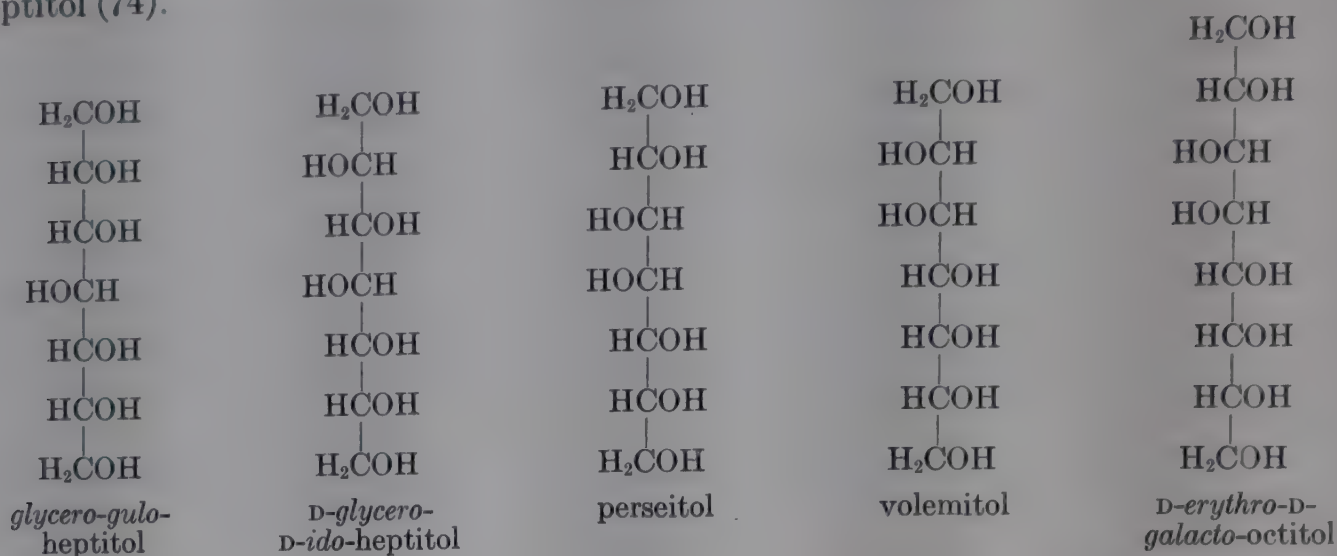
L-Iditol occurs in the berry of the mountain ash along with sorbitol. Catalytic reduction of L-idose forms L-iditol (86). Reduction of L-sorbose forms both L-iditol and sorbitol; the latter may be removed by fermentation to facilitate recovery of the L-iditol.

D-Talitol is formed by catalytic reduction of D-altrose (128). It also is formed from D-mannitol through the 1,2:5,6-diacetonate by the following sequence (127).



Higher Sugar Alcohols

Only a few straight-chain polyols with seven or more carbon atoms are considered in this article. Treatment of glucose with hydrogen cyanide, followed by hydrolysis to the acid, internal esterification to the lactone, and reduction produces through the epimeric heptoses, the two synthetic heptitols, *glycero-gulo-heptitol* and *D-glycero-D-ido-heptitol* (74).

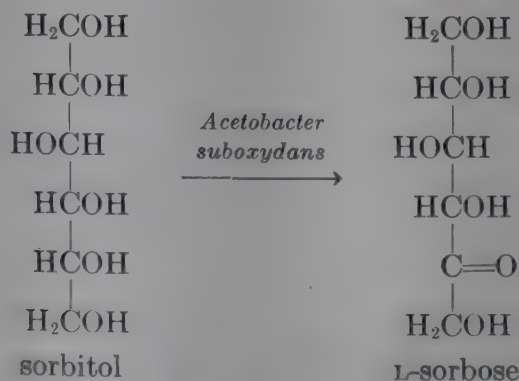


Perseitol occurs in the avocado (1–2%). It may be synthesized by reducing the heptose obtained from *D*-mannose by the cyanohydrin synthesis. Reduction of the *D*-mannoheptulose, which also occurs in the avocado, yields both *perseitol* (27) and *volemitol* (85). *Volemitol* is found in the mushroom, in the roots of several species of primrose and in red and brown algae (21,82).

D-erythro-D-galacto-Octitol is found in small quantities in the avocado, along with the corresponding octulose (27).

Reactions

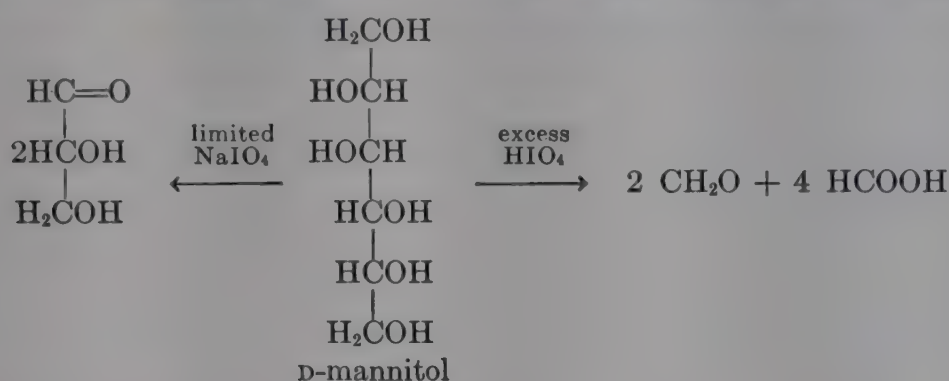
Oxidation. Oxidative attack on the polyols can range from slight to extensive and can be specific or general. Careful oxidation with aqueous bromine yields mixtures of aldoses and ketoses. Thus sorbitol is converted to a mixture of *D*-glucose, *D*-fructose, *L*-gulose, and *L*-sorbose (134). In the commercial synthesis of ascorbic acid (qv), the intermediate *L*-sorbose is obtained from sorbitol by fermentation with *Acetobacter suboxydans* (136).



The same organism as well as *Acetobacter xylinum* converts erythritol to *L*-erythrulose, *D*-arabitol to *D*-xylulose, *D*-mannitol to fructose, and *D*-talitol to *D*-tagatose. Dulcitol and xylitol are not attacked significantly. These results are generalized in the case of the more specific *Acetobacter suboxydans* (61) by Hudson-Bertrand rules which state that in a *cis* glycol with a *D*-configuration, a secondary hydroxyl adjacent to a pri-

mary hydroxyl is oxidized to a ketone (14). Reducing sugars result from the action of hydrogen peroxide in the presence of ferrous salts on erythritol, mannitol, dulcitol, or sorbitol. Oxidation of sorbitol with oxygen in the presence of a platinum-on-charcoal catalyst leads to L-glucose as well as small amounts of gluconic and glucuronic acids (63). Exposure of sorbitol or D-mannitol in aqueous solution to gamma or cathode rays promotes oxidation to the corresponding aldoses as well as chain degradation to D-arabinose (141). Oxidation of dulcitol with dilute nitric acid leads to mucic acid.

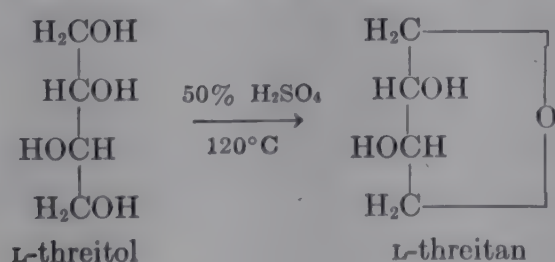
The carbon chain in polyols is broken by oxidation with lead tetraacetate or periodic acid. These reagents, because of their attack on the carbon-carbon bond between atoms bearing hydroxyl groups, are extensively used in determining the structures of sugars, sugar alcohols, and related compounds. Secondary alcohol groups are converted to formic acid while methylol groups yield formaldehyde. Thus D-mannitol is converted to four moles of formic acid and two moles of formaldehyde. It is also possible to conduct the reaction so that only partial degradation occurs by using limited quantities of periodate (108). Oxidative cleavage of D-mannitol, for example, occurs primarily at the threo linkage between carbons 3 and 4 and leads to D-glyceraldehyde.



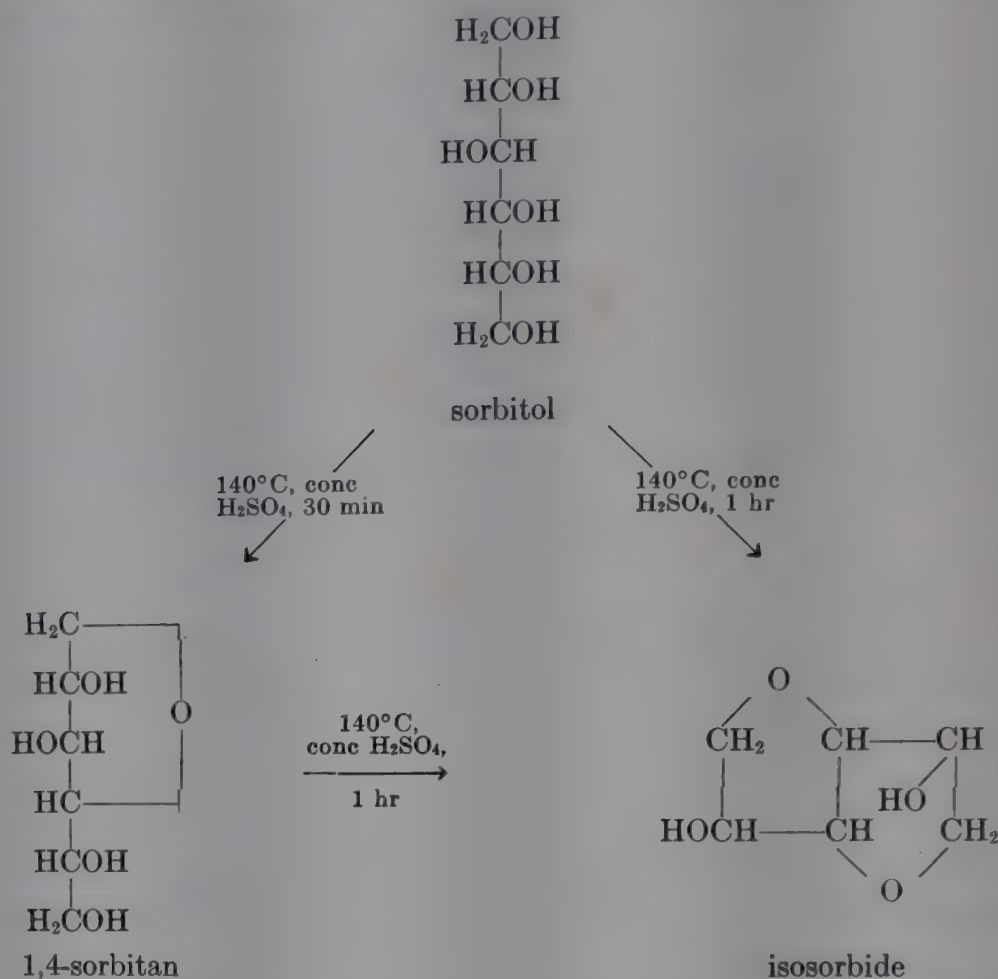
Permanganate, manganese dioxide, chromic acid, and nitric acid completely oxidize polyols to carbon dioxide.

Reduction. Sorbitol and mannitol are each converted by the action of concentrated hydriodic acid to secondary iodides (2- and 3-iodohexane). The results of this reduction were used in early proofs of structure of glucose and fructose with formation of this straight-chain carbon compound from the hexitols indicating the presence of a similar straight carbon chain in the monosaccharides (97). Catalytic hydrogenolysis of the polyols results in breaking of both carbon-to-carbon and carbon-to-oxygen bonds. Thus hydrogenolysis of sorbitol leads to the formation of glycerin, ethylene glycol, propylene glycol, erythritol, and xylitol (28). Glycerin and ethylene glycol also are formed by the hydrogenolysis of xylitol (60).

Anhydrization. The higher straight-chain polyols can undergo loss of one or more molecules of water internally to form cyclic inner ethers. The tendency to form external ethers between two polyol molecules is quite small. Nomenclature of anhydro derivatives is illustrated by those derived from the hexitols; monoanhydro internal ethers are called *hexitans*, while the dianhydro derivatives are called *hexides*. Internal anhydrization can occur under the influence of heat alone or in the presence of mineral acid catalysts. Thus, L-threitan is obtained by treatment of L-threitol with



50% sulfuric acid (24,75). Both mono- and dianhydrization have been observed with xylitol (25,54). When sorbitol is heated for a short time with about 1% sulfuric acid as catalyst, 1,4-sorbitan is obtained (116). Heating for double the reaction time leads to 1,4:3,6-dianhydrosorbitol (isosorbide) (68). Isosorbide can be obtained also by acid-catalyzed dehydration of either 1,4-sorbitan or 3,6-sorbitan (67).



Anhydrization of mannitol and iditol under similar conditions leads, respectively, to isomannide and isoioidide.

Two naturally occurring hexitans are known, polygalitol (1,5-sorbitan) and styracitol (1,5-mannitan). Styracitol has been prepared directly from D-mannitol by prolonged refluxing with concentrated hydrochloric acid (43); on shorter heating with hydrochloric acid, 1,4-mannitan is formed.

Esterification. Both partial and complete esters of sugar alcohols are known. The most important method for the preparation of partial fatty esters involves the interaction of polyols and fatty acids at 150–250°C (52). During direct esterification of the sugar alcohols, anhydrization occurs to varying degrees. Thus esterification of sorbitol with stearic acid leads to a mixture of stearates of sorbitan and isosorbide as well as of sorbitol. The degree of anhydrization in the resulting product is dependent upon the conditions of esterification. Unanhydrized esters may be prepared by reaction with acid anhydrides or acid chlorides or by ester interchange reactions. In general, use of an excess of these reagents leads to esterification of all hydroxyl groups. Completely substituted formate esters have been prepared from pentitols and hexitols by reaction with concentrated formic acid in the presence of phosphorus pentoxide (109).

Primary hydroxyl groups react with esterifying reagents appreciably more rapidly than secondary hydroxyls. As a consequence, it is possible to prepare ester derivatives

involving only the primary hydroxyls, as in the synthesis of the 1,6-dibenzenesulfonate of D-mannitol with benzenesulfonyl chloride in pyridine at 0°C (113).

The action of hydrochloric acid on polyols leads to some replacement of hydroxyl groups with chlorine as well as anhydrization. Thus, treatment of sorbitol with dry hydrogen chloride in acetic acid at 130–140°C leads to the formation of both isosorbide and a monochloro derivative (31). Heating mannitol with fuming hydrochloric acid in a sealed tube at 100°C results in the replacement of the primary hydroxyl groups with chlorine and in the formation of anhydrized products with and without chlorine (89,90).

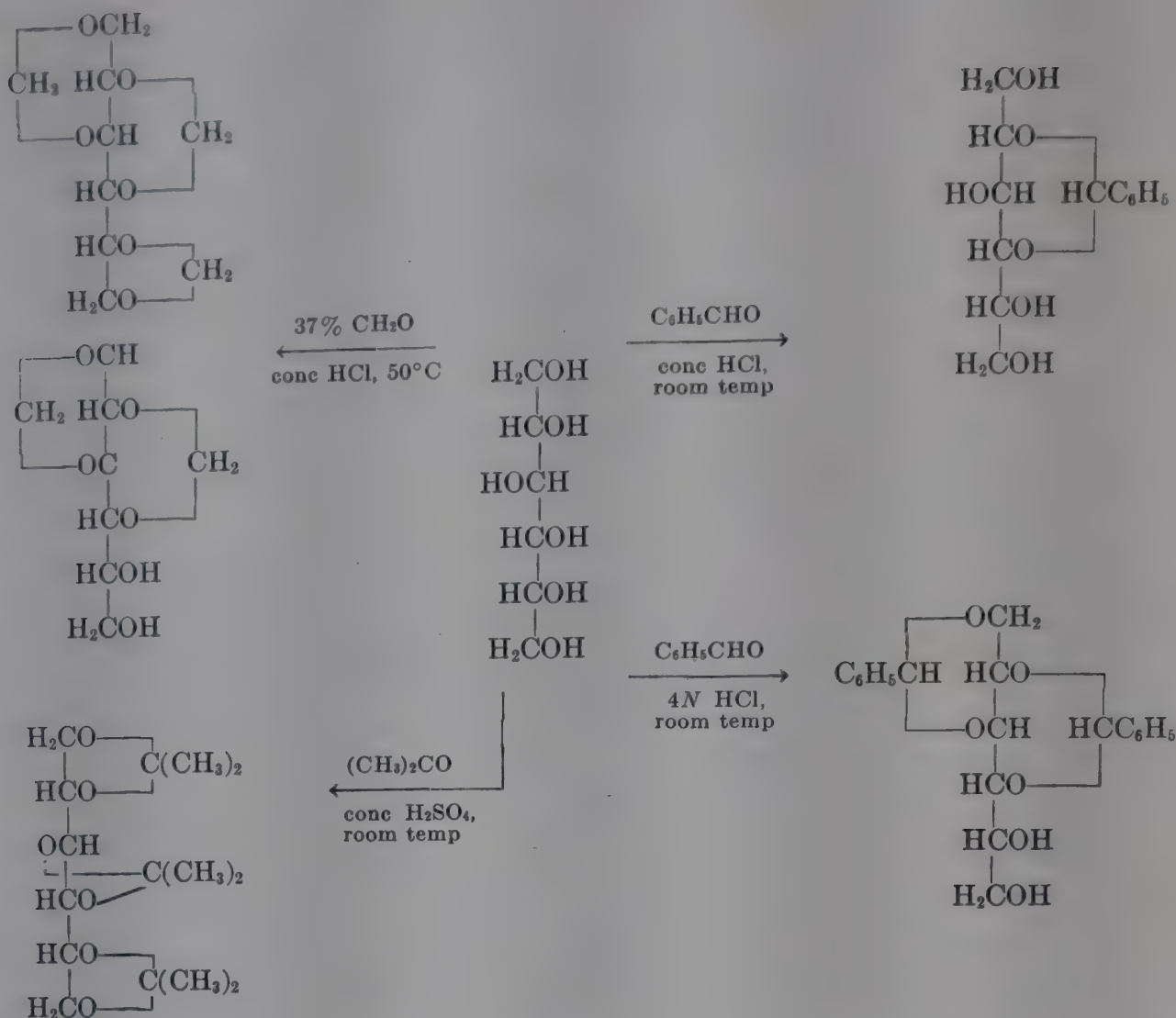
Mannitol hexanitrate is obtained by nitration of mannitol with mixed nitric and sulfuric acids. Similarly, nitration of sorbitol using mixed acid produces the hexanitate when the reaction is conducted at 0–3°C while at –10 to –75°C the main product is sorbitol pentanitate (132).

Aqueous solutions of boric, germanic, arsenic, telluric, tungstic, or molybdic acids or their salts form complexes with the sugar alcohols which involve the formation of ester linkages. Such complex formation increases the acidity of the inorganic acids and strongly enhances the optical rotation of the polyols. These complexes are usually stable only in solution, although crystalline monoborates of mannitol and dulcitol are known. Crystalline tri(benzeneboronate) derivatives are obtained by the reaction of sorbitol, mannitol, or dulcitol with benzeneboronic acid, $C_6H_5B(OH)_2$ (126).

Etherification. The reaction of alkyl halides with sugar polyols in the presence of aqueous alkaline reagents generally results in partial etherification. Thus a tetra-allyl ether is formed on reaction of D-mannitol with allyl bromide in the presence of 20% sodium hydroxide at 75°C (146). Treatment of this partial ether with metallic sodium to form an alcoholate, followed by reaction with additional allyl bromide, leads to hexa-allyl D-mannitol (93). Complete methylation of D-mannitol occurs, however, by the action of dimethyl sulfate and sodium hydroxide (47). Some selectivity for etherification of primary groups is achieved with triphenylmethyl chloride (trityl chloride) by the conversion of xylitol to 1,5-di-O-tritylxylitol in pyridine at room temperature (143). Completely substituted trimethylsilyl derivatives of polyols, distillable in vacuo, are prepared by interaction with trimethylchlorosilane in the presence of pyridine (121).

A type of etherification of commercial importance is the reaction of olefin oxides (epoxides) with polyols to produce polyoxyalkylene ether derivatives. Epoxides used include ethylene oxide and propylene oxide, and epichlorohydrin. The products of oxyalkylation have the same number of hydroxyl groups per mole as the starting polyol; for example, ethylene oxide converts $-OH$ to $-O(CH_2CH_2O)_nH$. A poly-substituted carboxyethyl ether of mannitol has been obtained by the interaction of mannitol with acrylonitrile followed by hydrolysis of the intermediate cyanoethyl ether (71), $-OH \rightarrow -OCH_2CH_2COOH$.

Acetal Formation. In common with other glycols, the sugar alcohols react with aldehydes and ketones to yield cyclic acetals and ketals. These derivatives are discussed in a comprehensive review (10). If the hydroxyl groups involved in acetal or ketal formation are adjacent, five-membered rings are formed, but if the reacting hydroxyls stand in a 1,3-relationship, six-membered rings result. From the hexitols, mono-, di-, or triacetals or ketals may be obtained, depending on reaction conditions. Some of the products of the reaction of sorbitol with formaldehyde (91), benzaldehyde (133,140), and acetone (22) are shown.



The acetals are formed under acidic conditions and, in general, are stable toward bases, oxidation, and reduction. Acetal formation is extensively used to protect hydroxyl groups during transformations in the polyol and carbohydrate series since conditions for the formation and removal of the cyclic acetal linkages are relatively mild and proceed without inversion of configuration at asymmetric centers.

Isomerization. Isomerization of sorbitol, D-mannitol, L-iditol, and dulcitol occurs in aqueous solution in the presence of hydrogen under pressure and a nickel-kieselguhr catalyst at $130\text{--}190^\circ\text{C}$ (145). In the case of sorbitol, D-mannitol, and L-iditol, a quasi-equilibrium composition is obtained regardless of starting material. The approximate equilibrium concentrations found are 41.4% sorbitol, 31.5% D-mannitol, 26.5% L-iditol, and 0.6% dulcitol.

Analysis

Analytical separation of the sugar alcohols from each other and from similar materials such as carbohydrates is best accomplished by paper or column chromatography. Sorbitol, for example, is readily separated from erythritol, glycerol, and other polyols by chromatography on paper using butanol-water as developing solution (115). Paper electrophoresis of polyols and carbohydrates in molybdate (23), tellurate, germanate (99), or borate solution also enables useful separations. Silicate adsorbents are of particular value in column chromatographic separation of polyols and sugars (81). Methods for separation such as selective solution or fractional crystallization are difficult with the sugar alcohols. Mannitol and dulcitol, however, may be separated from

more soluble polyols by crystallization from concentrated aqueous ethyl alcohol and identified by their melting points after recrystallizing from water.

Separated polyols may be detected by a variety of reagents. Reaction of sugar alcohols with ammoniacal silver nitrate on paper produces brown spots (69), vanillin in dilute perchloric acid forms gray-blue spots (51), and *p*-anisidine-phosphoric acid yields white spots (26,78). A mixture of sodium metaperiodate and permanganate, which yields a greenish-yellow spot, can be used to detect as little as 5–8 μ g of mannitol or erythritol (79). Identification of individual polyols by optical means is of little value because of the small rotations of the optically active polyols. Conversion to derivatives such as cyclic acetals, acetates, or trimethylsilyl derivatives, offers a means both of identifying individuals as well as effecting separations of polyol mixtures. Sorbitol hexaacetate has been readily separated from a mixture of polyol acetates by gas-liquid chromatography(36). Sorbitol is detected and determined in wine and vinegar by precipitating it with *o*-chlorobenzaldehyde forming the tris(*o*-chlorobenzylidene) derivative (87). Pyridine forms an insoluble molecular compound with sorbitol which is useful in isolating and identifying this polyol from natural sources as well as in industrial products (125).

Although nonspecific, one of the most valuable procedures for the quantitative analysis of polyols is the determination of hydroxyl number. This method involves reaction with acetic anhydride, followed by measurement of the acetic acid liberated. The concentration of a pure solution of sorbitol may be determined by means of the refractometer (105). The sugar alcohols also may be determined by periodate oxidation followed by measurement of the formaldehyde and/or formic acid liberated. The method has been applied to the determination of small quantities of sorbitol in biological fluids (8).

Manufacture of Sorbitol and Mannitol

Sorbitol is manufactured by catalytic hydrogenation of glucose using both batch and continuous hydrogenation procedures. Corn sugar is the most important raw material, but other sources of glucose, such as hydrolyzed starch, also may be used (33). In the continuous procedure, a 50% solution of dextrose in water is prepared and transferred to a mixing tank. The catalyst, nickel on diatomaceous earth, is added to the glucose solution and the resulting slurry is pumped to the reactor after being heated to about 140°C. Hydrogen, previously compressed to 175 atmospheres, is introduced into the reactor at a pressure of approximately 125 atmospheres concurrently with the sugar solution. Spent catalyst is collected on a filter and is separately regenerated for reuse. The sorbitol solution is purified in two steps: (1) by passage through an ion-exchange resin bed to remove gluconate as well as other ions and (2) by passage through an activated-carbon bed to remove trace organic impurities. The solution of pure sorbitol is concentrated in a continuous evaporator to a solution containing 70% solids which is sold under the trademark Sorbo, meeting USP XVI standards. Crystalline sorbitol is obtained by further concentration and crystallization. It is sold in both pelleted and powdered forms.

When invert sugar is used as a starting material, sorbitol and mannitol are produced simultaneously. Mannitol crystallizes from solution after the hydrogenation step due to its lower solubility in water. It is sold as a white, crystalline, free-flowing solid. Mannitol is available as an NF grade.

Extraction of mannitol from seaweed is a method of lesser importance commer-

cially. In one method starting with this source, whole seaweed is steeped at 20°C in water which has been acidified to a pH of 2 with sulfuric acid. After filtration, the extract is neutralized and made alkaline with lime, precipitating calcium, and magnesium sulfates, together with some colloids. The filtrate or centrifugate from this operation is dialyzed; mannitol and mineral salts pass through the semipermeable membrane. The dialyzate is concentrated and mannitol crystallizes from solution on cooling. If the weight ratio of mannitol to alkali chlorides in the dialyzate is less than 1, this ratio is attained by addition of pure mannitol before fractional crystallization is begun (4,5).

Uses

General: The hexitols and their derivatives are used in many diverse fields, including foods, pharmaceuticals, cosmetics, textiles, polymers, and other areas. See Alkyd resins; Bakery processes and leavening agents; Complexing agents; Confectionery; Cosmetics; Pharmaceuticals; Textile technology; Urethan polymers.

Aqueous sorbitol solutions are hygroscopic and are used as humectants, softeners and plasticizers in many different types of formulation. The hygroscopicity of sorbitol solutions is less than that of glycerin, but more than that of sugar solutions. The value of sorbitol in solution as a humectant is in its ability to stabilize the rate of moisture variation, thereby preventing rapid gain or loss of water. In crystalline form, sorbitol does not absorb moisture greatly below the level of about 70% relative humidity. Above this level sorbitol is deliquescent and will dissolve in absorbed water. Mannitol is considerably less hygroscopic in its crystalline form. Many applications of mannitol take advantage of its low hygroscopicity and its resistance to occlusion of water.

Another property of hexitols generally, and of sorbitol in particular, is the ability to sequester iron, copper, and aluminum ions in aqueous solution.

Mannitol has a mild laxative effect. Laxation due to sorbitol is less than that due to mannitol (34). The laxative threshold for sorbitol varies somewhat from person to person, but most individuals can ingest as much as 40 grams per day in divided doses before the laxative effect occurs (96,123).

The partial fatty acid esters of the hexitols, usually anhydriized, find extensive use in surface-active applications such as emulsification, wetting, detergency, and solubilization. Anhydriized sorbitol or mannitol moieties are versatile building blocks which confer hydrophilic properties on surfactants containing them. The less expensive sorbitol derivatives are used more extensively than the analogous mannitol compounds which also have value as surfactants. Fatty acid esters of hexitans are oil soluble and tend to form water-in-oil (w/o) emulsions. In fact, the sorbitan mono- and sesquioleates are among the most efficient w/o emulsifiers known.

The hydrophilic character of sorbitan fatty esters is enhanced by attachment of polyoxyethylene chains. As the polyoxyethylene chain length is increased, water solubility increases and oil solubility decreases. Hexitan fatty esters with long polyoxyethylene chains tend to form o/w emulsions.

Foods. Sorbitol imparts to frozen desserts body and texture, as well as some sweetness. Sorbitol is used in frozen desserts for diabetics because it is slowly absorbed from the intestine and is metabolized as fructose, a carbohydrate that requires less insulin than ordinary sugars (39). The slow rate of absorption of orally administered sorbitol, followed by its conversion to fructose in the liver, results in a prolonged slow supply of fructose which is considered to be of advantage to the diabetic (123).

For frozen desserts for special dietary use, Food and Drug Administration regulations permit sorbitol to be used as a stabilizer and nutritive sweetener in quantities of up to 15 grams per average serving (37). In the manufacture of sugarless chewing gum, both mannitol and crystalline sorbitol provide the water-soluble solids. A 70% solution of sorbitol in water is used in this application to provide the proper plasticity. Sorbitol resists fermentation to acids by microorganisms in the mouth and therefore is believed not to contribute to the incidence of dental caries (58,110–112). In artificially sweetened canned fruit, addition of sorbitol syrup, besides providing body, allows smaller quantities of saccharin to be employed for sweetening. Sorbitol has the property of reducing the undesirable aftertaste of saccharin (135). In low-calorie soft drinks, sorbitol finds use as a bodying agent, often in conjunction with an artificial sweetening agent such as sodium cyclohexylsulfamate. In addition, sorbitol sequesters metal ions in canned soft drinks. Sorbitol has been shown to sequester iron and copper ions in wines, thereby preventing cloudiness due to compounds of these metals (13).

In candy manufacture, sorbitol is used in conjunction with sugars to increase shelf life. It is used in making fudge, candy cream centers, soft and grained marshmallows, and in other types of candy where softness depends upon the type of crystalline structure. The function of sorbitol in this application is in retarding the solidification of sugar often associated with staleness in such candy. In butter creams, an additional benefit is involved in flavor improvement due to its sequestering action on trace metals. Sorbitol may be used in diabetic chocolates. Sorbitol is used as a humectant and softener in shredded coconut, having a decided advantage over the invert sugar often used, since darkening of the product does not occur. A small quantity of sorbitol, such as the 70% aqueous solution, added to peanut butter has been shown to reduce dryness and crumbliness and improve spreadability.

Sorbitan fatty esters and their polyoxyethylene derivatives are used as shortening emulsifiers. In cakes and cake mixes emulsification of the shortening is improved, resulting in better cake volume, texture, grain, and eating qualities. These emulsifiers are used in icings and icing bases as well as in pressure-packed synthetic cream-type toppings. In ice cream they confer improved body and texture. They are employed primarily to provide dryness and improved aeration. Polyoxyethylene(20) sorbitan monooleate and the corresponding tristearate are used as emulsifiers either separately or as blends in ice cream and other frozen desserts.

Pharmaceuticals. Mannitol finds its principal use in pharmaceutical applications. It is used as a base in chewable, multilayer, and press-coated tablets of vitamins, antacids, aspirin, and other pharmaceuticals. It provides a sweet taste and masks the unpleasant taste of drugs such as aspirin. Tablets containing mannitol retain little moisture because of its low affinity for water.

Sorbitol finds use as a bodying agent in pharmaceutical syrups and elixirs. The use of sorbitol in cough syrups reduces the tendency of bottle caps to stick due to crystallization of the sugar present. Enhanced stability is conferred by sorbitol in aqueous preparations of medicaments such as vitamin B₁₂ (12), ascorbic acid (49), and aspirin (19). Inclusion of sorbitol in aqueous suspensions of magnesium hydroxide prevents flocculation and coagulation even when subjected to freeze-thaw cycles. Crystalline sorbitol is used as an excipient where it gives a cool and pleasing taste due to its negative heat of solution.

A major pharmaceutical use of polyoxyethylene sorbitan fatty acid esters is in the solubilization of the oil-soluble vitamins A and D. In this way, multivitamin prepara-

tions can be made which combine both water- and oil-soluble vitamins in a palatable form.

Sorbitan sesquioleate emulsions of petrolatum and wax are used as ointment vehicles in skin treatment. In topical applications, the inclusion of both sorbitan fatty esters and their polyoxyethylene derivatives modifies the rate of release and promotes the absorption of antibiotics, antiseptics, local anesthetics, vasoconstrictors, and other medicaments from suppositories, ointments, and lotions. Polyoxyethylene(20) sorbitan monooleate, also known as Polysorbate 80 (USP XVI), has been used to promote absorption of ingested fats from the intestine (72). Mannitol hexanitrate is used as a vasodilator in the treatment of hypertension. The manufacture of vitamin C starts with the conversion of sorbitol to L-sorbose.

Cosmetics. Sorbitol is widely used in cosmetic applications, both as a humectant in which it retards the loss of water from o/w type creams, and as an emollient. It is useful in both brushless and lather-type shaving creams as a humectant and plasticizer. It is incorporated in many toothpaste formulas, as the vehicle, to the extent of 25–35%. This usage is based on its alkali stability, sweetness, humectant, and plasticizing properties.

Emulsions of fatty and petroleum based substances, both oils and waxes, of the o/w type are made using blends of sorbitan fatty esters and their polyoxyethylene derivatives. Mixtures of polyoxyethylene(20) sorbitan monostearate (Polysorbate 60) and sorbitan monostearate are typical examples of blends which are used for lotions and creams. Both sorbitan fatty acid esters and their polyoxyethylene derivatives are particularly advantageous in cosmetic uses because of their very low skin irritant properties. Sorbitan fatty ester emulsifiers for w/o emulsions of mineral oil are used in hair preparations of both the lotion and cream type. Polyoxyethylene(20) sorbitan monolaurate is useful in shampoo formulations. Derivatives such as sorbitan monopalmitate and polyoxyethylene(20) sorbitan monooleate emulsify fluorinated propellants used in pressure-packed hair sprays, deodorants, and shaving creams. Polyoxyethylene sorbitan surfactants also are used for solubilization of essential oils in the preparation of colognes and after-shave lotions.

Textiles. In textile bleaching or scouring solutions, which are strongly alkaline, sorbitol sequesters iron and copper ions. Sorbitan fatty acid esters and their polyoxyethylene derivatives are used both to emulsify textile treating chemicals and, by themselves, as finishes for textile processing. Polyoxyethylene(20) sorbitan monolaurate and its homologs are used as antistatic agents on textiles; they probably function by retaining sufficient moisture on the fabric to enable dissipation of static electricity by conduction. Friction of yarns and fibers can be controlled by applying blends of sorbitan fatty acid esters with other surfactants. Sorbitan monopalmitate and monostearate, together with other surfactants, serve as fabric softeners and textile size plasticizers. Polyoxyethylene derivatives of sorbitol and other polyols are used in viscose spinning baths to improve the properties of viscose rayon extruded in the form of filaments and films. Sorbitan monooleate is used in drycleaning detergents, often in conjunction with an anionic surfactant.

Polymers. Sorbitol, together with other polyhydric alcohols such as glycerin or pentaerythritol, can serve as the polyol component of alkyd resins and rosin esters for use in protective coatings and core binders. Linoleate and other unsaturated fatty acid esters of sorbitol and sorbitan find use as drying oil components. The polyoxypropylene derivatives of sorbitol have found extensive use as polyol components of

polyurethane resins, particularly for rigid urethane foams. In this application sorbitol derivatives with short polyoxypropylene chain lengths (eg, polyoxypropylene(10) sorbitol) are combined with a diisocyanate such as toluene diisocyanate, together with blowing agents, catalysts, and other additives, to prepare foams. Low-density (2 lb/cu ft) polyurethane foams made with polyoxypropylene sorbitols are used for their insulating properties, while those of higher density are used for their structural characteristics. The foams prepared with polyoxypropylene sorbitols have high crosslinking densities, resulting in good dimensional stability and good humid-ageing characteristics. As the number of polyoxypropylene units attached to sorbitol increases above about fourteen, the products become suitable for use in semirigid and resilient foams, coatings, and elastomers. Sorbitan and isosorbide esters may be used as plasticizers for vinyl resins and other polymers. In combination with various metal salts, sorbitol is used as a stabilizer against heat and light in polyvinyl chloride resins.

Miscellaneous Uses. Sorbitol is used in flexible glues, cork binders, and printers' rollers, frequently in combination with glycerin, to confer strength and flexibility as well as stability to humidity change. The high viscosity imparted by sorbitol in these applications is often desirable because it improves the mechanical strength and temperature resistance of the products (57). Glue-type products in which sorbitol is used include bookbinding, and magazine and paper tape adhesives. Sorbitol in conjunction with sugars, glycerin or propylene glycol has been used in tobacco as a component of casing solutions to add moisture retention properties. Sorbitol is used as a plasticizer in water-soluble carboxymethyl cellulose and amylose films. As a component in alkaline etching baths for aluminum, sorbitol helps eliminate scale formation on the surfaces of aluminum and aluminum alloys.

Mannitol has been used as an antioxidant and stabilizer for trivalent chromium ions in electroplating solutions. It also has been used in soldering fluxes because of its ability to form complexes with metallic oxides. Mannitol is used to stabilize perborates. Incorporated with ammonium borate in electrolytic condensers, it decreases power loss, increases breakdown voltage, and improves electrical properties. Mannitol is an antioxidant for photographic developers such as amidol and Metol (registered trademark of Zinsser & Co.). Mannitol has been used in bacteriological media for the identification of various microorganisms. Dulcitol also is used as a component of bacteriological media.

Polyoxyethylene derivatives of sorbitol and sorbitan fatty acid esters, usually in blends with anionic surfactants, are used as emulsifiers for insecticides, herbicides, and other pesticides. Oil emulsions for spraying dormant trees and fruits are prepared using these surfactants. Blends of sorbitan fatty acid esters and their polyoxyethylene derivatives are used to make w/o emulsions for use as hydraulic fluids. Other blends of these types of sorbitan surfactants are used to obtain o/w emulsions of wax for use in impregnating wood for pencils. Similar blends of sorbitan surfactants also are used to suspend pigments in water-based paints and in pigment pastes to keep the dispersions uniform. Organogels can be formed with ethylene glycol, nitrobenzene, vegetable oils, and other organic liquids using di- or tribenzylidenesorbitol as gelling agents.

Sorbitan monooleate functions as a corrosion inhibitor. Polyoxyethylene derivatives of sorbitan fatty acid esters serve as antistatic agents for phonograph records. In the explosives industry, mannitol hexanitrate is used as an initiator in blasting caps. Nitration of glycerin-ethylene glycol solutions of sorbitol yields low-freezing, liquid, high-explosive mixtures of value for dynamite formulas.

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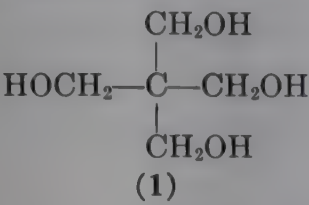
OTHER POLYHYDRIC ALCOHOLS

The most important of the alcohols discussed here is pentaerythritol. "Trimethylolethane," "trimethylolpropane," and dipentaerythritol are widely used industrial compounds.

Pentaerythritol.....	589	"Trimethylolpropane".....	595
Dipentaerythritol.....	593	1,2,4-Butanetriol.....	595
Tripentaerythritol.....	593	1,2,6-Hexanetriol.....	595
"Trimethylolethane".....	594	Anhydroenneaheptitol.....	596

Pentaerythritol

Pentaerythritol (1), or PE, is a tetrahydric neopentyl alcohol (2,2-bis(hydroxymethyl)-1,3-propanediol) which has found widespread use in the resin, plastics, and explosives industries. Pentaerythritol was discovered accidentally by Tollens (29) in 1882 as a by-product of the reaction between impure formaldehyde and barium hydroxide. Subsequent investigation led Tollens and his coworkers (30) to the conclusion that the pentaerythritol was the product of the reaction between formaldehyde and acetaldehyde, the latter being present as an impurity in the formaldehyde.



Properties. Pentaerythritol is an odorless, white, crystalline compound. It is nonhygroscopic, practically nonvolatile, and stable in air. It melts at 261–262°C, sublimates on heating under reduced pressure, and boils at 276°C/30 mm. Its density is 1.396 g/ml. Pentaerythritol is moderately soluble in cold water and freely soluble in hot water; it has only limited solubility in alcohols and other organic liquids (see Table 1) (3). Heat of combustion is 660 kcal/mole approximately; heat of formation, 226.6 kcal/mole (27); heat of vaporization, 22 kcal/mole, approximately, (15); heat of sublimation, 31.4 kcal/mole (23).

The high melting point of pentaerythritol, its slight solubility in water and alcohols, and the ready reactivity of its four hydroxyl groups have been attributed to the compact symmetrical structure of the molecule.

Table 1. Solubility of Pentaerythritol

Solvent	Temperature, °C	Solubility, g/100 g solvent	Temperature, °C	Solubility, g/100 g solvent
water	25	7.23	97	77.2
methanol (100%)	25	0.75	50	2.1
methanol (65%)	25	3.0	50	8.1
ethanol (100%)	25	0.33	50	1.0
ethanol (65%)	25	3.1	50	8.0
<i>n</i> -butylamine	25	16	78	16
dimethyl sulfoxide	25	4.5	90	30
ethanolamine	25	16.5	100	44.5
ethylene glycol	25	1.0	100	12.9
formamide	25	1.7	100	21.3
glycerol	25	0.8	100	10.3
pyridine	25	1.1	100	5.7
tetrahydrofurfuryl alcohol	25	0.2	100	3.7
acetone	56	<1.0		
amyl acetate	100	<1.0		
benzene	80	<1.0		
carbon tetrachloride	78	<1.0		
diethyl ether	68	<1.0		
dioxane	100	<1.0		
furfural	100	<1.0		
nitrobenzene	100	<1.0		
petroleum ether	71	<1.0		

In one industrial process for the production of pentaerythritol (25), formaldehyde and acetaldehyde in the molar ratio of about 4.4:1 are reacted in the presence of a 25% lime slurry for two hours, during which time the temperature is not allowed to rise above 50°C. Sodium carbonate is added to the reaction mixture to precipitate calcium carbonate. The reaction mixture, which contains pentaerythritol, polypentaerythritols, sodium formate, and suspended calcium carbonate, is then filtered to separate the calcium carbonate. The filtrate is concentrated by heating under reduced pressure and cooled to precipitate pentaerythritol and dipentaerythritol. Following filtration, the filtrate is processed to separate sodium formate and additional amounts of pentaerythritol. The filter cake is dissolved in hot water to form a concentrated solution which is passed through ion exchange columns to remove sodium formate and then is cooled. The pentaerythritol that precipitates is isolated, washed, and dried. Dipentaerythritol and additional amounts of pentaerythritol are recovered from the filtrate by processes involving fractional crystallization. The technical product obtained by this procedure may be purified by recrystallization from hot water and isolation of the pentaerythritol crystals between 70 and 180° C (40).

Analysis and Grades. The analysis of pentaerythritol involves the assay of pentaerythritol content as well as the measurement and characterization of the impurities present. The analysis of technical pentaerythritol generally includes the following determinations: pentaerythritol content, melting range, hydroxyl content, ash content, acidity, moisture content, water solubility, color, and physical state.

The most accurate and reliable method for determining pentaerythritol content is the benzal method. This procedure is based on the reaction of pentaerythritol with benzaldehyde to form its dibenzylidene acetal, a well-defined crystalline compound that is relatively insoluble in a dilute aqueous methanolic solution of hydrochloric acid containing benzaldehyde, and the subsequent gravimetric determination of this acetal.

The hydroxyl content of technical pentaerythritol, which serves as an indication of reactivity, is determined by acetylating the product with an excess of acetic anhydride in pyridine containing a small amount of water. The amount of unreacted anhydride is then measured by titration with sodium hydroxide solution.

Standard analytical procedures are used for the other determinations.

More than 80% of the pentaerythritol sold in the United States is sold as technical material that contains 85–90% of pentaerythritol and 10–15% of di- and higher pentaerythritols. Monopentaerythritol, which contains 98–99% of pentaerythritol, and the highly purified nitration grade of pentaerythritol account for the remainder of the sales.

Economic Aspects. U.S. production of pentaerythritol has increased tremendously since the manufacture of the technical product was begun in 1938. By 1941 production had increased to 2 million pounds. Under the impetus of World War II, production soared to more than 13 million pounds in 1945, much of the pentaerythritol being used in the manufacture of explosives. Production of pentaerythritol has continued to increase, reaching more than 36 million pounds in 1950, 61 million pounds in 1955, and 64 million pounds in 1959. Throughout the period from 1943 through 1959 the price of pentaerythritol has been relatively stable, ranging from 27¢ to 34¢ per pound for the technical grade (32). The price in 1962 was 29¢ per pound.

At the present time more than 90% of pentaerythritol production goes into surface-coating compositions, alkyd resins accounting for approximately 70%, and rosin esters for 20–25% of sales. Approximately 1% of the pentaerythritol produced is

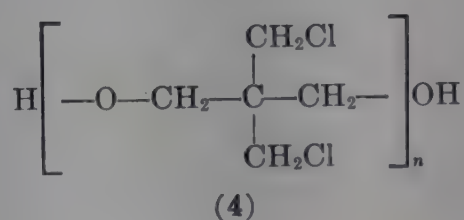
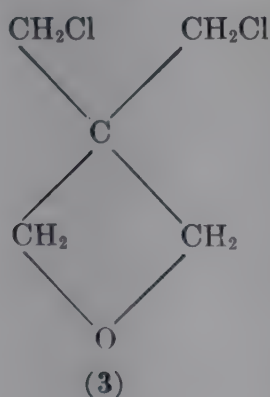
used in the manufacture of the explosive PETN (pentaerythritol tetranitrate). The remainder is used in the manufacture of plasticizers, waxes, lubricants, polymeric materials, and surface-active agents.

Uses. Pentaerythritol finds its principal use in the surface-coating field. Medium- and long-oil-length alkyd resins prepared from pentaerythritol, dibasic acids, and drying or semidrying oils or fatty acids are widely used in compositions that dry rapidly to form surface coatings with high gloss, excellent water and alkali resistance, and good ageing characteristics. In short-oil-length alkyd resins, pentaerythritol is usually employed in combination with a less functional polyhydric alcohol, for example, a glycol, to prevent premature gelation. These alkyd resins, when prepared from semidrying- or nondrying-oil fatty acids, are used with urea- and melamine-formaldehyde resins in baking enamels for metal finishes or with nitrocellulose in lacquers. To these coatings the pentaerythritol contributes improved hardness, gloss and gloss retention, color stability, and water resistance (see Alkyd resins).

Pentaerythritol-based rosin esters are used in a variety of products including paints, varnishes, lacquers, printing inks, floor coverings, and adhesives. Synthetic drying oils derived from pentaerythritol and drying-oil or semidrying-oil fatty acids are widely used in the formulation of paints, enamels, varnishes, putties and caulking compounds, linoleum cements, and core oils.

Pentaerythritol esters of fatty acids containing from 2–12 carbon atoms are used commercially as plasticizers (qv) for polyvinyl chloride resins (20). Such esters also show promise as lubricants (8,55) and as components of dietetic foods (62). Esters prepared from long-chain fatty acids are useful as synthetic waxes and as surface-active agents. Polyoxyalkylene ethers of pentaerythritol have proved useful as surface-active agents (qv) and as components of foamed polyurethane resins (see Urethan resins).

Pentaerythritol can be converted into 3,3-bis(chloromethyl)oxethane (3), and from this can be obtained a polyether (4) (Penton, made by Hercules Powder Co.).



This product (4) is characterized by excellent corrosion resistance and high dimensional stability. It is being used in the production of molded pipes, gears, and valves, and as a metal coating (6,7,28) (see Polyethers).

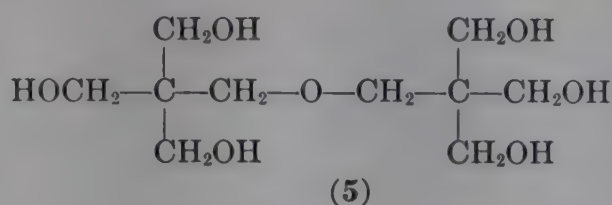
Polyspiroacetal resins (see Acrolein), prepared by the reaction between pentaerythritol and polyfunctional aldehydes, such as acrolein, methacrolein, crotonaldehyde, and glutaraldehyde, are finding application as electrical insulators, as surface-coating materials, as films and fibers, and as crosslinking agents for polyamides and polyesters (4,6,26).

Pentaerythritol has been employed alone or in combination with metal salts or epichlorohydrin as a heat stabilizer for polyvinyl chloride resins (45,49,51,58,59).

Pentaerythritol has also found use in fire-retardant surface coatings (see Fire-resistant chemical treatments). Exposed to high temperatures, these coatings froth and swell to produce a solid, noncombustible residue which serves to protect the substrate from fire (48,52,57).

Dipentaerythritol

Dipentaerythritol (DiPE) (5) is obtained as a by-product of the reaction of formaldehyde and acetaldehyde under alkaline conditions to form pentaerythritol. It is present to the extent of 10–15% in the technical grades of pentaerythritol and is separated from the latter by procedures based on differences in solubility in either water or alcohols (16,21,56).



Dipentaerythritol is a white, odorless, crystalline compound. It is nonhygroscopic, stable in air, and practically nonvolatile. Pure dipentaerythritol melts at 221–222.5°C; the technical grade, which contains 10% of pentaerythritol and tripentaerythritol, melts at about 200°C. The heat of combustion of dipentaerythritol is 1848 kcal/mole. The product is less soluble than pentaerythritol in water and organic solvents (see Table 2). The density of dipentaerythritol is 1.365 g/ml (3).

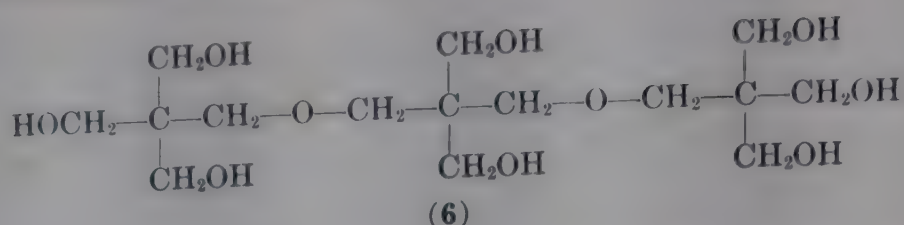
Table 2. Solubility of Dipentaerythritol

Solvent	Temperature, °C	Solubility, g/100 g solvent	Temperature, °C	Solubility, g/100 g solvent
water	30	0.30	50	0.90
methanol	25	0.26	65	0.6
glycerol	25	<0.1		
acetone	25	<0.1		
benzene	25	<0.1		

Dipentaerythritol is used principally in the preparation of drying oils, rosin esters, and alkyd resins. Surface-coating compositions derived from dipentaerythritol are more viscous and faster drying than the corresponding pentaerythritol products, and they form coatings that have improved hardness, gloss, and durability. Fatty acid esters of dipentaerythritol have been used as plasticizers for polyvinyl resins, as lubricants for aircraft engines, and as waxes (8,20,63). Dipentaerythritol is used in the preparation of intumescent fire-retardant compositions (57).

Tripentaerythritol

Tripentaerythritol (TriPE) (6) is also a by-product of the pentaerythritol reaction. It is separated from pentaerythritol by fractional crystallization and is purified by recrystallization from solutions containing formic, sulfuric, or hydrochloric acid (44). Tripentaerythritol is usually sold as a technical product containing 90–92% of tripentaerythritol, the remainder being pentaerythritol and dipentaerythritol.

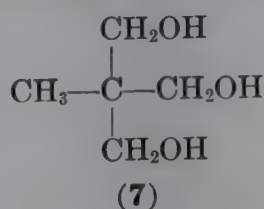


Triptaerythritol is a white, nonvolatile compound that is very slightly soluble in water and organic solvents. The purified product melts at 248–250°C; the technical product, at 230–240°C. Triptaerythritol has a density of 1.30 g/ml; its heat of combustion is 3070 kcal/mole (3).

Triptaerythritol is used principally in the preparation of surface-coating materials. It is particularly useful in the manufacture of fire-retardant surface coatings.

Trimethylolethane

“Trimethylolethane” (2-hydroxymethyl-2-methyl-1,3-propanediol) (7) is a trihydric neopentyl alcohol, which is used principally in the surface-coatings field.



Trimethylolethane is an odorless, somewhat hygroscopic, white, crystalline solid that melts at 200.5–202°C. The pure product boils at 283°C; the technical product decomposes before its boiling point is reached. Trimethylolethane is soluble in water and in the lower aliphatic alcohols; slightly soluble in ketones, ethers, and esters; and insoluble in aliphatic and aromatic hydrocarbons (14). The product is nontoxic and nonirritating to animals.

Trimethylolethane is prepared by the condensation of formaldehyde with propionaldehyde in the presence of an alkaline condensation catalyst, such as sodium hydroxide or lime. The reaction can be expressed by a series of two equations, similar to those for the formation of pentaerythritol.



The process is generally carried out by reacting 1 mole of propionaldehyde with about 3.5 moles of formaldehyde and 1.1 moles of sodium hydroxide at a temperature between 25 and 40°C (18). The product is recovered from the reaction liquor by extraction with an organic solvent, such as acetone (46), methyl isobutyl ketone (54), or propanol (43), and by crystallization from the solvent extract. One process from which a high yield of very pure trimethylolethane is obtained calls for the extraction of the reaction liquor with butyl or amyl alcohol, reextraction of the resulting extract with water, and crystallization of trimethylolethane from the aqueous solution (53).

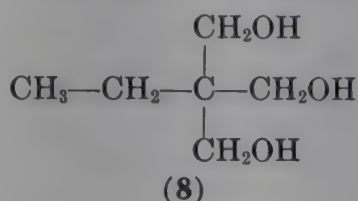
At the present time several million pounds of trimethylolethane are sold annually in the United States at a price of about 30¢ per pound.

Most of the trimethylolethane produced is used in the production of alkyd resins. Industrial finishes containing these resins dry rapidly to form coatings that are characterized by excellent hardness, color and gloss retention, alkali resistance, and durability. Synthetic drying oils obtained by the esterification of trimethylolethane with drying-oil and semidrying-oil fatty acids are used in the production of varnishes and

other surface-coating compositions. Esters prepared from trimethylolethane and saturated fatty acids have proved valuable as plasticizers, waxes, emulsifiers, and lubricants (1,8,14). Polyesters derived from trimethylolethane may be used in the production of polyurethane resin foams.

Trimethylolpropane

“Trimethylolpropane” (2-ethyl-2-hydroxymethyl-1,3-propanediol) (8) is a white, crystalline polyhydric alcohol containing three primary alcohol groups.



Trimethylolpropane melts at 57–59°C and boils at 160°C/5 mm. It is a hygroscopic compound which is soluble in water, alcohols, and acetone and insoluble in aliphatic and aromatic hydrocarbons (5).

Trimethylolpropane is prepared by the condensation of formaldehyde with butyraldehyde under alkaline conditions. Because of its complete solubility in water, trimethylolpropane cannot be crystallized satisfactorily from the aqueous reaction mixture. It is usually separated from the metal formates and other by-products of the reaction by distillation under vacuum (35) or by treatment with an alcohol, such as 2-propanol (43), amyl alcohol (34), or cyclohexanol (38).

Several million pounds of trimethylolpropane are sold annually in the United States at a price of about 31¢ per pound.

Trimethylolpropane is used principally in the production of polyurethane resin foams. Polyesters prepared from trimethylolpropane and dibasic acids are reacted with aromatic diisocyanates to form tough rigid or flexible foams that are resistant to heat and to chemicals (5). Alkyd resins derived from trimethylolpropane have good color and color retention, flexibility, adhesion, and hardness (17). Esters of trimethylolpropane are used as plasticizers, synthetic drying oils, and lubricants (1,8).

1,2,4-Butanetriol

1,2,4-Butanetriol (1,2,4-trihydroxybutane), $\text{HOCH}_2\text{CH}_2\text{CHOHCH}_2\text{OH}$, a hygroscopic syrup with a sweet taste, boils at 119°C/0.17 mm and has a viscosity at 25°C of 1227 cps and a density of 1.184 g/ml. It is completely miscible with water and ethanol. It is relatively nontoxic and nonirritating to laboratory animals (13).

1,2,4-Butanetriol may be prepared by the hydrogenation of 1,4-dihydroxy-2-butanone in the presence of a molybdenum sulfide catalyst (37). 1,4-Dihydroxy-2-butanone is obtained by hydration, with an acid or mercury catalyst, of 1,4-butyndiol (see Alcohols, unsaturated). 1,2,4-Butanetriol may be used as a solvent, a humectant, or as an intermediate in the production of explosives, pharmaceuticals, and resinous products.

1,2,6-Hexanetriol

1,2,6-Hexanetriol (1,2,6-trihydroxyhexane), $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CHOHCH}_2\text{OH}$, is a liquid trihydric alcohol, prepared by hydrolyzing acrolein dimer (see Acrolein) and then hydrogenating the resulting 2-hydroxyadipaldehyde (26).

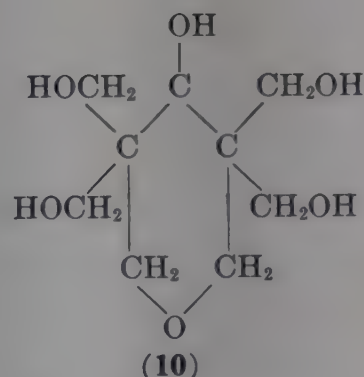
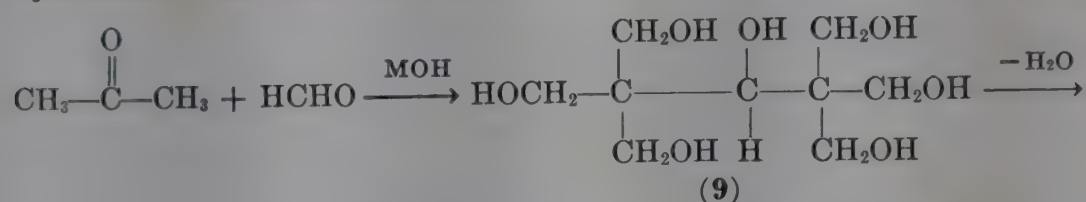
1,2,6-Hexanetriol is a stable liquid that boils at 178°C/5 mm and has a viscosity at 20°C of 2584 cps. It is completely miscible with water. It is relatively nontoxic and nonirritating to laboratory animals (31).

1,2,6-Hexanetriol has been used as a humectant-plasticizer for animal glues and for casein, zein, and other water-soluble products. It reacts with dibasic acids to form slow-drying, soft alkyd resins. Polyesters and polyethers derived from 1,2,6-hexanetriol may be used in the production of polyurethane foams and elastomers.

Anhydroenneaheptitol

Anhydroenneaheptitol (10), or tetrahydro-3,3,5,5-tetrakis(hydroxymethyl)-4-pyranol, is a hygroscopic compound that melts at 138–139°C and that is soluble in water, alcohols, and ketones. Anhydroenneaheptitol is relatively nontoxic and nonirritating to laboratory animals.

Anhydroenneaheptitol is prepared by the condensation of formaldehyde with acetone under alkaline conditions to form an intermediate heptitol (9), which is then dehydrated. The reactions can be expressed by the following equations.



This process proceeds to completion without the isolation of an intermediate product. Because of its complete solubility in water, anhydroenneaheptitol cannot be crystallized satisfactorily from the aqueous reaction mixture. It is usually separated from the metal formates and other by-products of the reaction by distillation under vacuum or by extraction with an alcohol, such as 2-propanol (24a,45a). The product is generally sold as a solution that contains 25–30% of water.

Anhydroenneaheptitol may be used in the preparation of explosives, pharmaceuticals, surfactants, drying oils, and alkyd resins.

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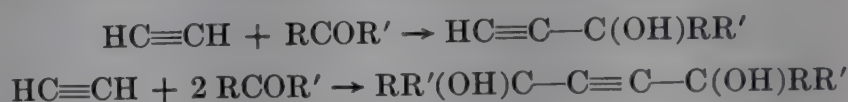
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ALCOHOLS, UNSATURATED

This article discusses monohydric alcohols and dihydric alcohols (glycols) obtained by the reaction of acetylene with carbonyl compounds. Acetylene can react with one or two molecules of a carbonyl compound as follows:



With formaldehyde as the carbonyl compound, primary alcohols are obtained; with other aldehydes, secondary alcohols; and with ketones, tertiary alcohols.

	RCOR'	$\text{HC}\equiv\text{CH}$ plus $2 \text{RCOR}'$
$\text{R} = \text{R}' = \text{H}$ (formaldehyde)	$\text{HC}\equiv\text{C}-\text{CH}_2\text{OH}$ (propargyl alcohol)	$\text{HOH}_2\text{C}-\text{C}\equiv\text{C}-\text{CH}_2\text{OH}$ (2-butyne-1,4-diol)
$\text{R}' = \text{H}$, $\text{R} = \text{alkyl or aryl}$ (aldehydes)	$\text{HC}\equiv\text{C}-\text{CHROH}$ (secondary alcohols)	$\text{HORHC}-\text{C}\equiv\text{C}-\text{CHROH}$ (secondary glycols)
$\text{R}, \text{R}' = \text{alkyl or aryl}$ (ketones)	$\text{HC}\equiv\text{C}-\text{CRR}'\text{OH}$ (tertiary alcohols)	$\text{HORR}'\text{C}-\text{C}\equiv\text{C}-\text{CRR}'\text{OH}$ (tertiary glycols)

The above acetylenic compounds can be converted by semihydrogenation into the corresponding ethylenic compounds. The ethylenic compound corresponding to propargyl alcohol, allyl alcohol, $\text{H}_2\text{C}=\text{CHCH}_2\text{OH}$, an important industrial chemical, is manufactured by a different route; see Allyl compounds. The ethylenic compounds corresponding to the other acetylenic alcohols are discussed here.

Propargyl alcohol, 2-butyne-1,4-diol, and 2-butene-1,4-diol.....	598
Bibliography.....	614
Secondary and tertiary acetylenic and ethylenic alcohols and glycols.....	618
Bibliography.....	634

PROPARGYL ALCOHOL, 2-BUTYNE-1,4-DIOL, AND 2-BUTENE-1,4-DIOL

Propargyl alcohol.....	599
2-Butyne-1,4-diol.....	602
Manufacture of propargyl alcohol and 2-butyne-1,4-diol	609
2-Butene-1,4-diol	611
Bibliography.....	614

Propargyl Alcohol

Propargyl alcohol (2-propyn-1-ol), $\text{HC}\equiv\text{CCH}_2\text{OH}$, is a colorless, moderately volatile liquid possessing a mild, geraniumlike odor. It is used in the manufacture of drugs and agricultural products, in the stabilization of halogenated solvents, and as a corrosion inhibitor, particularly in oil well acidizing operations. Its three reactive centers have resulted in its use as an intermediate in the preparation of many new derivatives.

Propargyl alcohol was first synthesized by Henry in 1872 from β -bromoallyl alcohol (1). It was first prepared by reaction of acetylene and formaldehyde by Reppe in Germany (2). Commercial quantities of propargyl alcohol are available in the United States from a large-scale unit by General Aniline & Film Corporation.

PHYSICAL PROPERTIES

Propargyl alcohol is infinitely miscible with the following: water, benzene, chloroform, 1,2-dichloroethane, ethanol, ethyl ether, acetone, *p*-dioxane, tetrahydrofuran, and pyridine. Appreciable heat is evolved when propargyl alcohol is mixed with pyridine. It is soluble to a limited extent in carbon tetrachloride and is immiscible with aliphatic hydrocarbons. Some physical properties of propargyl alcohol are listed in Table 1.

Propargyl alcohol forms an azeotrope with water which boils at 97°C. The azeotropic mixture has a composition of 45 parts by weight of propargyl alcohol and 55 parts of water.

Commercially available propargyl alcohol has a minimum purity of 97%. Typical impurities in propargyl alcohol include formaldehyde, formals, and water. This product is shipped in steel containers.

CHEMICAL PROPERTIES

Propargyl alcohol is a stable compound. Under normal conditions, assay of commercial grade diminishes less than 1% on one year storage.

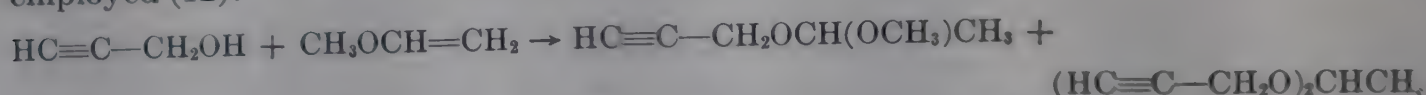
Table 1. Physical Properties of Propargyl Alcohol

melting point, °C	-52		
refractive index, n_D^{20}	1.429-1.431		
specific gravity, 20/4°C	0.948-0.949		
viscosity at 20°C, cps	1.68 ^a		
dielectric constant, ϵ	24.5 ^a		
specific heat at 20°C, cal/(g)(°C)	0.616 ± 0.004 ^a		
flash point, open cup, °F	97 ± 5		
molar heat of combustion, kcal	413.6		
molar heat of vaporization at 112°C, kcal	10.06 ^a		
boiling point, °C,	115		
vapor pressure data ^a			
°C	mm Hg	°C	mm Hg
20	11.6	80	225.2
30	20.6	90	335.9
40	35.4	100	490.3
50	58.6	110	701.7
60	94.2	112.3	760.0
70	147.6		

^a Data obtained from Technical Oil Mission microfilms (4).

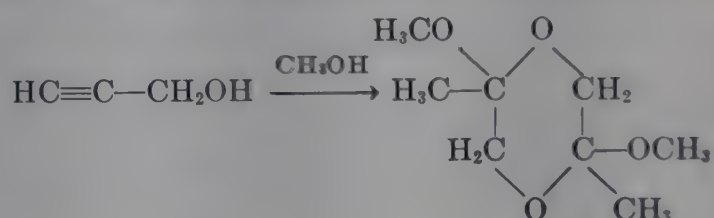
The chemical properties of propargyl alcohol result from the three reactive centers of the molecule. The hydroxyl group undergoes the characteristic reactions of primary alcohols; the triple bond gives the addition reactions of unsaturated compounds; and the methine hydrogen permits reactions at this active center.

Reactions of the Hydroxyl Group. Propargyl alcohol undergoes ester (5-7) and ether (2) formation quite readily. The hydroxyl group can be oxidized to the aldehyde, yielding propiolaldehyde (propargylaldehyde), $\text{HC}\equiv\text{CCHO}$, by reaction with manganese dioxide in acid solution (8) or by reaction with chromic acid (9). Propargyl alcohol is oxidized to propiolic acid, $\text{HC}\equiv\text{CCOOH}$, in good yields, by electrolytic oxidation (10,11). It adds to methyl vinyl ether, in the usual manner of alcohols, to form a mixture of acetals, the proportion depending upon the reaction conditions employed (12).



Reactions of the Triple Bond. The acetylenic linkage of propargyl alcohol may be partially reduced by hydrogen under suitable catalytic conditions to allyl alcohol or completely reduced to 1-propanol. Under specific catalyst conditions, reduction is accompanied by a rearrangement which yields propionaldehyde (3,13-16).

This propargyl alcohol linkage undergoes addition reactions with water to form acetol, $\text{CH}_3\text{COCH}_2\text{OH}$ (13,14); with alcohols to form cyclic acetals (3,14,17,18),



with sodium bisulfite to form disodium 3-hydroxy-1,2-propanedisulfonate (12); with hydrogen chloride to form β -chlorallyl alcohol, $\text{H}_2\text{C}=\text{CClCH}_2\text{OH}$; with phosphorus trihalides to form 3-halo-1-propynes; with thionyl chloride in pyridine to form 3-chloro-1-propyne (3,14,19-23).

Secondary amines will add across the triple bond of propargyl alcohol in the presence of an inert solvent with manganese dioxide catalyst. Simultaneous oxidation and addition occur to yield β -aminoacroleins, $\text{R}_2\text{NHC}=\text{CHCHO}$ (24).

Reactions of the Methine Hydrogen. Propargyl alcohol may be trimerized via the methine hydrogen to yield a mixture containing approximately equal parts of 1,2,4- and 1,3,5-tris(hydroxymethyl)benzene (13). The methine hydrogen will react readily with aldehydes to yield 2-butyne-1,4-diol in the case of formaldehyde and unsymmetrical diols in the case of other aldehydes (12,14,25,26). Oxidative coupling of propargyl alcohol occurs with air or oxygen and results in coupling of two molecules to form 2,4-hexadiyne-1,6-diol (13,14,19,27). This is readily reduced to form 1,6-hexanediol, an important intermediate for polyamides and polyurethanes. The methine hydrogen is replaced by chlorine by reaction of hypochlorite in alkaline solution to yield 3-chloro-2-propyn-1-ol (13,14). Propargyl alcohol reacts with dialkylamines and formaldehyde via the methine hydrogen to yield 4-dialkylamino-2-butyne-1-ols (12). The methine hydrogen of propargyl alcohol will react with Grignard reagents, such as $\text{CH}_3\text{CH}_2\text{MgBr}$. The ethyl Grignard reaction product of propargyl alcohol reacts with carbon dioxide to yield 4-hydroxy-2-butyric acid (19,28).

Analysis. Propargyl alcohol is acetylated in pyridine. After hydrolysis of the unreacted acetic anhydride, the solution is titrated with standard sodium hydroxide.

HEALTH AND SAFETY FACTORS

Propargyl alcohol is a primary skin irritant, but it is not a skin sensitizer. Adequate ventilation should be provided when appreciable quantities of vapor may be encountered.

Acute oral toxicity: $LD_{50} = 0.07$ ml/kg (white rats); 0.06 ml/kg (guinea pigs).

Like acetylene, propargyl alcohol is liable to spontaneous decomposition in the presence of certain chemicals and in certain temperature ranges (29). Propargyl alcohol should be made slightly acidic with acetic or succinic acid before distillation. Other precautions as discussed below under 2-Butyne-1,4-diol should be taken.

USES

Propargyl alcohol is used in the production of 2-aminopyrimidine, a key intermediate for sulfadiazine. There are two general approaches to the use of propargyl alcohol in the manufacture of sulfadiazine. Propargyl alcohol may be oxidized to propiolaldehyde using manganese dioxide or chromic acid. Propiolaldehyde is then condensed with a guanidine salt to form 2-aminopyrimidine (8,30,31).

An alternate synthesis is based on the reaction of propargyl alcohol with a dialkyl amine in the presence of manganese dioxide to yield β -dialkylaminoacrolein (24). The dialkylaminoacrolein compound is then reacted with a guanidine salt to give high yields of 2-aminopyrimidine (32). This method can also be used to obtain various substituted members of the pyrimidine series.

Propargyl alcohol is an effective inhibitor in preventing corrosion attack on steel by mineral acids (33–36). It is particularly effective in hydrochloric acid. It has found acceptance in the treatment of oil-producing wells with hydrochloric acid since its protective action is manifested at high temperatures. It has been shown that increasing the degree of unsaturation in a three-carbon linear alcohol (1-propanol, allyl alcohol, propargyl alcohol) is accompanied by an increasing degree of effectiveness of inhibition (35). Propargyl alcohol is most effective in this application at concentrations of 0.05–0.25%, based on anhydrous weight of acid.

Propargyl alcohol is unique among all monosubstituted acetylene derivatives in its ability to prevent hydrogen embrittlement of steel at very low concentrations (37).

Propargyl alcohol is used to stabilize chlorinated solvents, such as trichloroethylene, against decomposition and subsequent attack on metals (38,39). It is used either alone as the stabilizer or in conjunction with nitrogen-containing stabilizers such as pyrrole and substituted pyrroles. Concentrations of 0.005–0.25% have been suggested in this application. The ethers and esters of propargyl alcohol are also used as stabilizers for hydrocarbon solvents (40).

Propargyl alcohol is used in agriculture as a replacement for allyl alcohol in soil fumigant formulations. Propargyl alcohol is less phytotoxic than allyl alcohol (41) and, at the same time, more toxic than allyl alcohol to nematodes, fungi, and certain bacteria.

Propargyl alcohol is used commercially as an intermediate in the manufacture of propargyl bromide by reaction with phosphorus tribromide and is used to manufacture propargyl chloride by reaction with phosphorus trichloride.

Compounds possessing hypnotic activity are manufactured from propargyl alcohol. These are generally substituted propargyl carbinols (42,43).

The carbanilate of propargyl alcohol has been found to be very effective in the prevention of decay in Florida oranges (44).

2-Butyne-1,4-diol

Pure 2-butyne-1,4-diol, $\text{HOCH}_2\text{C}\equiv\text{CCH}_2\text{OH}$, usually referred to simply as butynediol, is a white, orthorhombic crystalline solid which turns slightly yellow on exposure to light and air. It is used in electroplating to produce bright, ductile nickel deposits; as a corrosion inhibitor in pickling baths; as a defoliation agent for cotton; and in paint and varnish remover formulations. Its three reactive centers make it a versatile chemical intermediate. Some derivatives are used as corrosion inhibitors in petroleum refining, as herbicides with selective action, as insecticides, as solid propellants of the polyurethane type, as textile auxiliaries, pharmaceuticals, or dye intermediates.

Butynediol was first synthesized by Jozitsch in 1906 from acetylene dimagnesium bromide and paraformaldehyde (45). It was later prepared by Reppe (46) by the high-pressure reaction of acetylene and formaldehyde which is still used in the first large-scale commercial unit built in the United States by General Aniline & Film Corporation (GAF) in 1956.

PHYSICAL PROPERTIES

Solid butynediol can be dissolved readily in water or aqueous acids, ethanol, and acetone. This product is also soluble to the extent of 10% or more in glacial acetic acid, 1,4-butanediol, butyrolacetone, Cellosolve (registered trademark of Carbide and Carbon Chemicals Co.), dioxane, ethyl acetate, methanol, methyl pyrrolidone, propargyl alcohol, pyridine, and tetrahydrofuran. It is sparingly soluble in diethyl ether and most chlorinated hydrocarbons and is essentially insoluble in benzene. Some physical properties of butynediol are listed in Table 2.

Butynediol is commercially available as 97% and 99% minimum purity solids and as a 35% aqueous solution. Typical impurities in butynediol include formaldehyde and propargyl alcohol. Solid butynediol is shipped in fiber drums.

CHEMICAL PROPERTIES

Solid butynediol in the dry state remains substantially unchanged for prolonged periods of time. Aqueous solutions are reasonably stable, although slight changes may be noted on long storage, especially in warm locations or when unduly exposed to air. Butynediol may be stored in mild steel, glass, Monel (registered trademark of International Nickel Co.), and stainless steel. Since alkynediols, in general, are liable to spontaneous decomposition, special caution is required to avoid contamination with many chemicals and exposure to the higher temperature ranges.

Multiple centers of reactivity in the butynediol molecule permit it to function in a variety of ways: (1) as a disubstituted acetylene, through classic additions to the triple bond, eg, hydrogen, water, halogens, halogen acids, alcohols, sodium bisulfite; (2) as a glycol, by replacing OH groups to form halogen compounds, esters, and ethers; (3) by trimerization, dimerization, and esterification to form cyclic compounds.

Hydrogenation. The acetylenic linkage of butynediol is easily reduced by catalytic hydrogenation to yield a variety of reaction products, depending on the

Table 2. Physical Properties of Butynediol

<i>Pure butynediol</i>	
melting point, °C	58
boiling point, °C	
1 mm Hg	105–107
10 mm Hg	140
100 mm Hg	194
760 mm Hg	238
flash point, °C	152
burning point, °C	158
heat of combustion, cal/g	6121
refractive indices, n_D^{25}	$\alpha = 1.450 \pm 0.002$ $\beta = 1.528 \pm 0.002$
density, g/ml	1.17
<i>Aqueous solution of butynediol (35%)</i>	
appearance	straw to amber colored liquid
solidification point, °C	<−7
specific gravity, 25/4°C	1.04–1.05
pH	4–6

catalyst, pH, temperature, etc, as discussed in some detail in the literature (46–57). In a continuous, high-pressure process at 40–100°C, strong catalysts, such as platinum or activated nickel on a porous carrier, produce the fully saturated product. Butynediol may be converted directly to furan using cobalt molybdate and high temperatures and pressure (58).

Isomerization. Butynediol isomerizes to hydroxymethyl vinyl ketone, $\text{H}_2\text{C}=\text{CHCOCH}_2\text{OH}$, a colorless liquid with an extremely pungent odor. This Meyer-Schuster rearrangement occurs on warming butynediol to 40–60°C in the presence of catalysts such as mercuric, silver, or cupric salts of strong acids (46,49,59,60). Yields of 50% have been reported (61), but the pure ketone polymerizes very quickly, especially in light, to form a gel and later a colorless, odorless, hard mass.

Many reactions of butynediol proceed through this isomerization mechanism. As a result of the neighboring carbonyl group, the double bond of hydroxymethyl vinyl ketone, is activated and very readily adds water, alcohols, phenols, carboxylic acids, amines, and other similarly reacting compounds.

Hydration. Butynediol is converted in 70–90% yield into 1,4-dihydroxy-2-butanone, $\text{HOCH}_2\text{COCH}_2\text{CH}_2\text{OH}$, by the addition of one mole of water (46,59,61–64). The reaction is catalyzed by mercuric salts at temperatures below 40°C. It proceeds via isomerization to hydroxymethyl vinyl ketone. The hydrated product has a tendency to self-condensation, making isolation somewhat difficult.

1,4-Dihydroxy-2-butanone can be easily reduced to 1,2,4-butanetriol, which has been proposed as an intermediate for explosives (61,63,65). The triol is also of interest in the manufacture of alkyds, polyurethanes, and polyesters; it may be dehydrated to 3-hydroxytetrahydrofuran which is of interest in the plasticizer field. If hydration of the hydroxymethyl vinyl ketone is not complete, or if the temperature is too high during reduction of the dihydroxybutanone, the formation of butane-1,2-diol is favored, and above 100°C the yield of the latter may be as high as 70%.

In the presence of ammonia and formaldehyde, 1,4-dihydroxy-2-butanone warmed at 70–80°C in aqueous solution with copper sulfate forms the copper salt of

β -chloroethylimidazole from which pure histamine can be obtained on treatment with alcoholic ammonia (46).

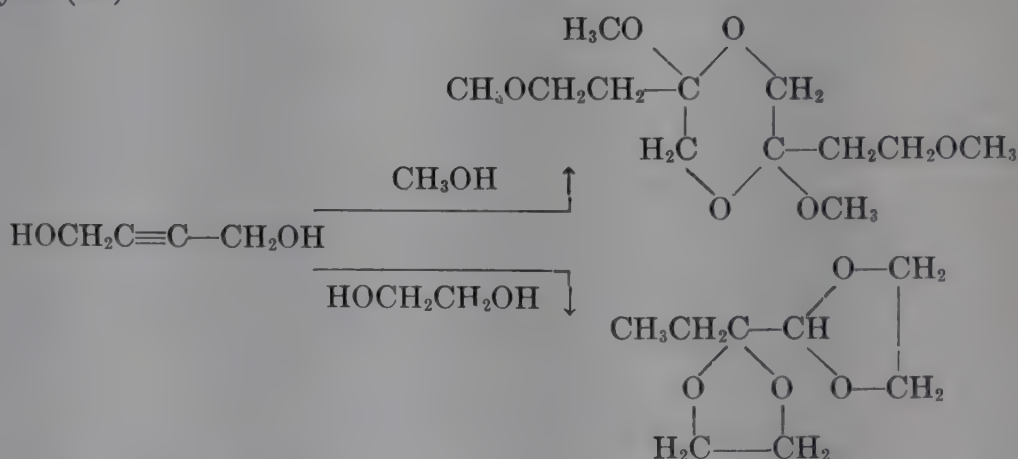
A method for the preparation of mono- or polyketones or polyketocarboxylic acids by reaction of butynediol with carbon monoxide and water in the presence of a carbonyl-type catalyst has been patented (66). These reaction products are reported to be of interest for the preparation of plastics, or as intermediates for plasticizers, lacquers, resins, textile assistants, and tanning agents.

Addition of Alcohols. The addition of alcohols in the presence of mercury salts does not lead to the expected ketal of 1,4-dihydroxy-2-butanone. Instead, butynediol first isomerizes to hydroxymethyl vinyl ketone and subsequently, one molecule of alcohol adds to the double bond to form the monoalkyl ether of 1,4-dihydroxy-2-butanone (46,59,63).



With methanol, the rate is so rapid that the intermediate vinyl ketone cannot be isolated, but, with higher alkyl alcohols, the intermediate product may be isolated. It has also been suggested that the reaction may take place through the formation of 1,4-dioxane which by saponification yields the 4-alkoxybutan-1-ol-2-one. On reduction, these alkoxyketones give the monoethers of butanetriol-1,2,4. Since water is present during the reaction, dihydroxybutanone is also formed in addition to the alkoxyhydroxybutanone.

In the absence of water, when butynediol is treated with acidic mercury or copper compounds in the presence of alcohols, complex cyclic ethers are formed; glycols give acetals of substituted glyoxals from which the glyoxals can be liberated by acid hydrolysis (46).



Various esters of α -hydroxybutyric acid, $\text{CH}_3\text{CH}_2\text{CHOHCOOR}$, have been prepared by heating butynediol at 200°C in an autoclave with an alcohol and zinc carbonate (46).

Addition of Sodium Bisulfite. Either one or two sulfonic acid groups can be added to the triple bond of butynediol (46). In the former case, unsaturated sulfonic acids are formed, in the latter, disulfonic acids (67). This reaction is especially interesting since, ordinarily, salts of sulfurous acid add only to those acetylene derivatives in which the triple bond is activated by adjacent carboxyl groups. Sodium 1,4-dihydroxy-2,3-butanedisulfonate is a highly water-soluble compound capable of giving reactions similar to those of glycols.

Trimerization. Butynediol can be trimerized to hexamethylolbenzene by heating in the presence of nickel catalysts and a suitable solvent. Use of triphenylphosphine-nickel carbonyl catalyst gives the best yields (59,61,68).

Reaction with Ammonia and Amines. The reaction of butynediol with primary amines is rather complex; the resulting compounds may be substituted vinyl derivatives or ketimines which are somewhat unstable (48,69). In aqueous solutions, using mercuric sulfate as catalyst, the reaction probably proceeds via hydration of the triple bond to give 1,4-dihydroxy-2-butanone as an intermediate. The reaction of two moles butynediol with one mole 1,4-diaminoanthraquinone to give the substituted imine has been patented (70).

In the case of secondary amines or heterocyclic compounds containing the $=\text{NH}$ group, the corresponding substituted vinyl derivative is formed, accompanied by polymerization and cyclization products. It is probable that these reactions also proceed via hydration of the triple bond.

Cyclic compounds are formed by reacting butynediol with ammonia or a primary amine over a heated catalyst (48,59,71).

Reactions with Halogens. Butynediol adds one equivalent of hydrogen chloride or hydrogen bromide to the triple bond at 70°C with concurrent replacement of a hydroxy group by halogen. The action of hydrogen chloride on melted butynediol (or in solution) gives the dichlorocrotyl alcohol, $\text{ClCH}_2\text{CH}=\text{CClCH}_2\text{OH}$, in high yield (61). 2,3-Diiodo-2-butene-1,4-diol is formed by warming butynediol with aqueous iodine, but a definite product could not be isolated from the action of elemental chlorine (47). 2,3-Dichlorobutane-1,4-diol has been prepared by passing hydrogen chloride through butynediol in aqueous acidic medium containing copper salts (72). The 4-halo-2-butyne-1-ol derivatives have also been prepared and recommended in the control of organisms in soil, such as fungi, wireworms, and root-knot nematodes (73).

The bromination of butynediol in different solvents has been studied (74). In carbon tetrachloride or dimethyl formamide, bis(2,3-dibromo-2-butene-1,4-diol) (67% and 51% yields, respectively) were formed; in acetic acid, 4-bromotetrahydro-3-furanone (70% yield).

Reaction with thionyl chloride can yield a dimeric cyclic sulfite ester (46), 1,3,4-trichloro-2-butene (59,61,75), and other reaction products. In the case of thionyl bromide, the formation of 1,2,2,4-tetrabromobutane has been reported (47). Reactions with inorganic acid halides under anhydrous conditions cause the hydroxyl groups to be exchanged for halogen atoms. 1,4-Dichloro-2-butyne is a particularly useful chemical intermediate. It also can be used to modify wool chemically and to alter the fiber's microbiological response (76).

The halogenated derivatives of butynediol are useful intermediates for many other compounds, one of the most interesting being diacetylene (butadiyne). Diacetylene may be prepared by adding 40% aqueous sodium hydroxide to 1,4-dichloro-2-butyne in alcohol, previously warmed to 75°C (46,61,77). Many reactions of diacetylene with alcohols, carbonyl compounds, mercaptans, and amines have been studied on a laboratory scale and some have been worked out for production (48).

Etherification. Aliphatic ethers of butynediol may be prepared by the action of alkyl sulfates, alkyl halides, or dialkyl sulfates (46,60,78). Carboxylic acids can be added to the triple bond of butynediol ethers (and esters) under the influence of copper salts, yielding unsaturated ethers (and esters) (46).

Aromatic ethers of alkynediols may be prepared by reaction of their esters with aromatic sulfonic acids (46). Several aryl ethers of butynediol have also been prepared by the action of the sodium derivatives of the appropriate phenol on 1,4-dichloro-2-butyne (47).

A polyacetal is formed by condensing butynediol with paraformaldehyde in the presence of *p*-toluenesulfonic acid as catalyst (79). This product may be vulcanized by warming with sulfur dichloride and the resulting sulfur-crosslinked polymer can range from an elastic mass to a clear friable product, depending on the proportion of sulfur dichloride used. Ether polymers of butynediol are reported to be formed by condensation of the glycol with a dialkyl acetal in the presence of a strong acid catalyst and heat. Typical polymers of this type are poly-2-butyne-1,4-dioxymethylene and poly-2-butyne-1,4-dioxypropylidene (80,81).

Esterification. Esters and polyesters of butynediol may be prepared by reaction with carboxylic acid anhydrides, carboxylic acid chlorides, or sulfonic acid chlorides (46,47,82). The acetylenic linkage in the phosphite esters is reported to impart valuable properties in insecticide-fungicide materials, resin-forming chemicals, lube-oil additives, and intermediates (83).

Unsaturated polyesters can be prepared by successively reacting phthalic anhydride with butynediol and cyclopentadiene or a homolog of the latter. These polyesters, when mixed with a vinyl compound, such as styrene, and polymerized, form suitable resins for lacquers, castings, and laminates (84).

The dibenzoate of 2-butyne-1,4-diol, which is reported to stabilize chlorinated hydrocarbons (85), has been prepared by esterifying butynediol with benzoyl halides (47,62). The disulfate of 2-butyne-1,4-diol may be prepared by sulfating butynediol with pyridine chlorosulfonic acid (86); the monosulfate results from treatment of the diol with sulfuric acid (82). The reductive acetylation of butynediol with acetic anhydride in the presence of lithium aluminum hydride to yield 1,4-diacetoxy-2-butene has also been described (87).

Haloacetic acid esters of butynediol exhibit specific biological activity as herbicides, aphicides, fungicides, defoliants, and the like (88).

Oxidation. Electrolytic oxidation of butynediol gives acetylenedicarboxylic acid (89,90), which has also been prepared in lower yield by treating the diol with an excess of chromic acid solution in acetone (75). The formation of malonic acid from butynediol and peroxyacetic acid has been described in the literature (91).

Reaction with Sulfur. Butynediol, heated under hydrogen pressure with powdered sulfur and a cobalt catalyst, produces a mixture of thiol compounds, principally 2-mercapto-tetrahydrofuran (92).

Reaction with Cyano Compounds. 1,4-Dicyanobutene can be prepared by reacting butynediol with hydrogen cyanide under pressure in the presence of cupric bromide, ammonium chloride, and copper (93). The reaction of butynediol with 3-chlorophenyl isocyanate and subsequent halogenation with thionyl chloride produces 4-chloro-2-butynyl *N*-(3-chlorophenyl)carbamate in 90% yield (94,95). The latter product is the herbicide, barbane (Carbyne, registered trademark of Spencer Chemical Company), a highly effective agent for the control of wild oats in grain, peas, and sugar beets.

Analysis. In the preferred method for assay for solid butynediol, the sample is acetylated in pyridine. Unreacted acetic anhydride is hydrolyzed with water, and the solution is titrated with standard sodium hydroxide (96).

For the assay of the 35% aqueous solution of butynediol, the sample is brominated in the presence of acid and mercuric sulfate. The excess bromine is reacted with potassium iodide solution and then titrated with thiosulfate. A blank is run and the amount of unsaturation determined by the difference in the titration of the blank and the test solution (96).

HEALTH AND SAFETY FACTORS

Pure butynediol is nonexplosive. However, small amounts of certain impurities may cause explosive decomposition upon distillation. Therefore, it is good practice to use a protective shield and goggles. Special care should be taken not to carry the distillation to completion. Under no circumstances should one distill butynediol which contains alkali or alkaline earth hydroxides, halides, etc, since decomposition can occur very easily under these circumstances. In strong acids, contamination with mercury salts can also result in violent decomposition.

In general, butynediol should not be treated with basic catalysts in the absence of a solvent at room temperature and still less so at elevated temperatures, otherwise, uncontrollable decomposition may occur. A good rule to follow when butynediol is used in a pressure vessel is to have only as much compound present that if it were replaced by an equivalent amount of acetylene at the same temperature and volume, a pressure of no more than 15 atm gage would be produced (97). This is especially prudent when the reaction is a new one.

Acute oral toxicity: $LD_{50} = 0.125$ g/kg (white rats); 0.125 g/kg (guinea pigs).

Butynediol is a primary skin irritant but does not appear to be a skin sensitizer. Every precaution should be taken to avoid physical contact with concentrated material. The compound does not usually sting or burn to give an indication of irritant effects. In case of accidental contact, the affected parts should be washed immediately with a large volume of water. Adequate ventilation should be provided.

USES

Electroplating. Butynediol and several of its derivatives are remarkably effective in producing bright, fine-grained electroplated deposits with appreciable increases in ductility (98–104). From 0.3–1.5 g butynediol per liter electroplating bath is commonly employed, often in combination with a sulfo-oxygen compound of the sulfonic acid type. Aeration and the addition of surface-active agents aid in obtaining pit-free nickel deposits. Butynediol is also used in copper plating.

Derivatives of butynediol reportedly used successfully as electroplating brighteners include acetic acid derivatives, eg, 1,4-diacetoxy-2-butyne, $HOOCCH_2-OCH_2C\equiv CCH_2OCH_2COOH$, and aliphatic or aromatic sulfonic acid derivatives, eg, 2-butyne-1,4-disulfonic acid, $HO_3SCH_2C\equiv CCH_2SO_3H$.

Pickling and Scale Removal. Butynediol appears to fulfill all requirements for the ideal inhibitor for mineral acids used in pickling baths for metals and alloys, especially iron and steel (105). It has been postulated (106) that butynediol polymerizes into a cyclic structure on the surface of the metal and that the freshly cleaned metal surface is chelated into the ring structure.

In normal pickling operations, butynediol in a concentration as low as 0.02% is effective for short exposures to hydrochloric acid or sulfuric acid or in blended formulations. Butynediol does not attack iron or steel. It is especially effective in lead-lined pickling tanks and in the removal of rust or oxide which contains carbonates. It does not appreciably decrease the rate of scale removal. Butynediol is outstanding in operations where a quick removal of the oxide layer is desired without loss of base metal. It is also used to advantage where it becomes necessary to interrupt a pickling operation or in the case of a temporary plant shutdown. An additional advantage is its tendency to decrease hydrogen gas evolution, lessening acid loss from spattering. In the pretreatment of steel pipe, butynediol-inhibited baths establish a better surface for subsequent lining with protective organic coatings (106).

Butynediol is also an effective corrosion inhibitor for sulfamic acid but is not recommended for use with nitric or phosphoric acids.

In the industrial removal of mineral scale from iron and steel by the use of strong acids, butynediol in minimum quantities effectively protects the clean metal areas, even when scale formation is very irregular. Its use may be adapted to solutions for the removal of scale from boilers and from milk, beer, and fruit processing equipment. Butynediol does not affect the rate of scale removal which is normally dependent on the thickness of the coating and on the accessibility of the kettle or pipe.

Stabilizer for Halogenated Hydrocarbons. Butynediol improves the service life of most commercial halogenated solvents in the presence of metals, light, heat, oxygen, or water. It is sparingly soluble in halogenated hydrocarbons but to a sufficient extent that it can act as a stabilizer for chlorinated solvents. For example, the addition of less than 0.5% butynediol to aqueous chlorinated solvents, eg methylene chloride, used in extruding cellulose triacetate, inhibits clogging and corrosion of the jets and other metal equipment (107). It can function as a corrosion inhibitor in drycleaning operations employing perchloroethylene. Butynediol has also been used with polymers and copolymers of vinylidene chloride to protect iron rollers and molds (108). In this application, butynediol not only has the effect of preventing corrosion of the metal but appears to reestablish the initial polish.

Petroleum Refining. Acetylenic alcohols and derivatives are currently used in oil well acidizing solutions and, more recently, in gas-sweetening operations. Derivatives of butynediol appear particularly valuable in the inhibition of corrosion due to dissolved gases, such as hydrogen sulfide, carbon dioxide or oxygen, in aqueous systems. In alkanolamine brine systems commonly used for removing acid gases from refinery streams, the condensation products of butynediol and polyethyleneamines effectively prevent filiform and pitting corrosion (109). In a field test in a refinery Girbitol unit, the reaction product of butynediol and tetraethylenepentamine appeared to control corrosion problems successfully.

Paint and Varnish Remover. Butynediol is a nonvolatile stripping agent for paint and varnish remover formulations (110). Old paint and lacquer coatings soften quickly when treated with an organic solvent containing butynediol in a concentration as low as 2% (96). The blistered paint is easily removed by scraping and, since butynediol is water soluble, the surface may be flushed clean with water.

Defoliation. Butynediol and certain of its esters are useful defoliants in the culture of cotton, castor beans, soy beans, nursery stock, and fruit trees (111).

Insecticide and Herbicides. Butynediol is indicated in the control and eradication of mites and ticks on chlorophyllaceous plants (112). Its action is ovicidal.

Butynediol is the basic raw material used in the synthesis of 4-chloro-2-butyne-1-*N*-(3-chlorophenyl)carbamate, a new chemical for the control of the weed, wild oats (94,95).

Polymerization Accelerator. In the emulsion polymerization of vinyl compounds and ethylidene chloride, butynediol can markedly accelerate the reaction (113). From 0.5 to 10% butynediol has been employed with the further advantage that the polymerization may be carried out at considerably lower temperatures. In certain copolymerizations, butynediol can also act as a chain regulator.

Crosslinking of Cotton. Cotton cellulose may be crosslinked with a four carbon chain by treatment with an aqueous solution containing 10% of the sodium salt of 2-butyne-1,4-dioxydisulfonate, $\text{NaO}_3\text{SOCH}_2\text{C}\equiv\text{CCH}_2\text{OSO}_3\text{Na}$, and 20% sodium hydrox-

ide (86). This causes no visible change from that induced by an alkali heat cure alone. Such crosslinked cotton has a lack of affinity for a direct cotton dye (Pontamine Fast Blue, Du Pont) but readily takes an acetate dye (Celliton Fast Yellow RRA, GAF). This may be explained by the blocking of the hydroxyl groups in the crosslinked cellulose. The conversion of cellulose into a space polymer also makes it essentially insoluble in Schweitzer's reagent (cuprammonium hydroxide).

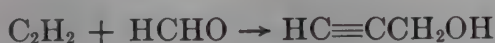
Polyurethanes. In studies on the use of glycols as chain extenders for urethane rubbers, butynediol has been found to impart particularly high tensile and tear strengths (114). Further, the glycol crosslinking technique permits liquid-phase processing without solvents. No gas formation occurs, and it is reported possible to mold massive bodies of any desired thickness directly from the reaction mixture. Polyurethanes of butynediol and hexamethylene diisocyanates have also been characterized (115).

Manufacture of Propargyl Alcohol and 2-Butyne-1,4-diol

The commercial synthesis of propargyl alcohol and butynediol in the U.S. and Germany is based on the work of Reppe and his co-workers in Germany (116–125). Both of these products can be formed by passing an aqueous solution of formaldehyde, along with a recycle stock containing formaldehyde, propargyl alcohol, and butynediol, down through a bed of copper acetylide catalyst cocurrent with flowing acetylene under pressure. An excess of formaldehyde is more favorable for the formation of butynediol,



whereas the formation of propargyl alcohol is favored by a high acetylene pressure and a low concentration of formaldehyde,



Propargyl alcohol is usually a by-product in this reaction, but its formation may be controlled to a degree by the operating conditions employed. The reaction products are separated and purified by distillation.

Plant Construction. The hazards involved in handling acetylene under pressure have been given prime consideration in the design and construction of the manufacturing plants (119,126).

Although no techniques have yet been found which will completely prevent the decomposition of acetylene, practical methods have been developed for so moderating acetylene decompositions that they do not develop into detonations.

The plant in Germany has been designed and built for working pressures up to 200 atm in order that slow decompositions of acetylene may be contained within the equipment (116–118,120–122). It has been considered to be impractical to build the plant to contain the pressure developed by a detonation (over 10,000 psi).

In Germany the reactors are stainless-steel towers, 58.5 ft high and 4.9 ft in diameter. An empty tower without cover weighs about 70 tons. Each reactor is equipped with (1) a liquid feed preheater, (2) a hot liquid–gas separator for disengaging hot liquors from gas at the foot of the reactor, (3) a gas cooler for cooling gas separated in the hot separator, and (4) a cold liquid–gas separator for removing liquid from the gas leaving the gas cooler. All of the towers are interconnected by common

lines to allow for flexible operations. Centrifugal pumps are employed for feeding and circulating solutions.

The Copper Acetylide Catalyst. A copper acetylide catalyst supported on a silicious carrier is employed in the manufacture of propargyl alcohol and butynediol (116–118, 121–123, 125, 127). The catalyst is generated in the reactors by reaction with formaldehyde and acetylene. This is desirable since it simplifies the handling of copper acetylide which is sensitive to shock, impact, and air.

Temperature peaks can occur very easily during the formation of the acetylide and should be avoided. Therefore, the concentration of acetylene in the cycle gas is increased gradually during the activation period. If the temperature tends to rise, nitrogen or water is added. Higher temperatures trigger the butynediol reaction which must be avoided as much as possible during the catalyst generation in order that a catalyst of uniform composition is produced throughout the reactors. The generation of the catalyst is completed when the acetylene concentration in the effluent gas is about the same as the gas going into the towers.

Plant Operation: Flow, Feed, and Products. Crude carbide acetylene is purified by washing successively with water, 8% sulfuric acid, chlorine water, and 10% sodium hydroxide. The water catches lime, the sulfuric acid removes ammonia, and the chlorine water oxidizes sulfur compounds which are taken up in the sodium hydroxide. Charcoal is used to reduce the chlorine content of the acetylene gas.

The acetylene is compressed and is passed into and through the reactors. The unreacted gas passes from the reactors to the hot liquid–gas separators, through the gas coolers, to the cold gas–liquid separators and finally back to the recycle pump. A portion of the gas is vented to prevent the build-up of inerts (nitrogen, carbon dioxide, etc) and undesirable gases (oxygen).

The liquid feed, composed of aqueous formaldehyde, recycle butynediol, propargyl alcohol, and formaldehyde, is pumped into the reactors. As the liquid passes over the catalyst, it reacts exothermically with the acetylene. An exothermic heat of reaction of 55 kcal/mole is calculated for the formation of butynediol from gaseous formaldehyde and acetylene. However, the quantity of heat which actually appears in the liquid phase and which must be removed amounts to only about 24 kcal/mole. This difference is due to the heat of solution of the butynediol, the heat of solution of the acetylene, and the heat required to raise the reaction solution to the operating temperature. The heat transferred to the acetylene also helps to remove some of it.

The gas and liquid pass through the reactors. The reaction products pass to the hot liquid–gas separator. The liquid is degassed, filtered, and is passed back to the feed makeup tank or is passed on to a second reactor, where it goes through a cycle similar to that just described.

The temperature control of the reaction towers is of special significance since the process proceeds satisfactorily only within a limited temperature range. Increases in temperature must be avoided since the formation of cuprene proceeds very rapidly in spite of the presence of inhibitors. This leads to rapid plugging, excess buildup of back pressure, and premature reactor shutdown.

The final product contains about 30–33% of butynediol, 0.5–4% of propargyl alcohol, 1% of methanol, 0.5–1% of formaldehyde, a small amount of involatile residue, and water.

Yields of butynediol in excess of 90% based on formaldehyde and 80% based on acetylene are achieved.

Workup of Product Solutions. The product from the butynediol-propargyl alcohol synthesis is passed to a multiplate distillation column. The vapor-liquid equilibrium for the propargyl alcohol-water system is such that the overhead concentration of propargyl alcohol from very dilute solutions is quite easy. The overhead from the still may contain 35–40% propargyl alcohol from very dilute feed solutions. The pot residue is forwarded for butynediol processing. The aqueous butynediol solution may be used "as is," or crystalline butynediol may be obtained by crystallization or vacuum distillation.

The overhead distillation product from the previous stripping operation is further processed to recover its propargyl alcohol content (128). This propargyl alcohol-water solution is reacted with acidified methanol. Upon distillation in a second stage, the overhead contains methanol reaction products, and the higher boiling propargyl alcohol azeotrope remains. In the third stage, benzene is added to the azeotrope and after distillation there remains an enriched propargyl alcohol solution, which in the fourth stage is distilled to an overhead of propargyl alcohol of about 99.5% purity.

2-Butene-1,4-diol

2-Butene-1,4-diol (butenediol), $\text{HOCH}_2\text{CH}=\text{CHCH}_2\text{OH}$, is a colorless, odorless stable liquid. The commercially available product is a clear amber liquid. It is used in the manufacture of insecticides, resins, and pharmaceuticals. It is the only olefinic glycol available in tank car quantities. Its active double bond and two primary hydroxyl groups have resulted in its use in preparing several new commercially available derivatives.

Butenediol was first synthesized by Prevost in 1926 by the hydrolysis of the diacetate of butenediol with barium hydroxide (129). It was first prepared by reduction of 2-butyne-1,4-diol by Reppe in Germany (130–132). Commercial quantities of butenediol are available in the United States from a large-volume production unit built by General Aniline & Film Corporation.

The first reported preparations of butenediol referred only to the trans isomer. In 1926, the synthesis of butenediol by means of a cumbersome sequence of reactions starting with erythritol was reported (133). In 1928, another preparation starting with butadiene was reported (134). The material obtained was identified in each case as *trans*-2-butene-1,4-diol and was reported to be free of the cis isomer.

Some years earlier, it had been shown that homologs of butynediol could, by partial hydrogenation, be converted to olefinic glycols (135). These products were principally cis isomers containing variable, but usually small, amounts of trans isomers (136). Acetylenic glycols were available from the reaction of acetylene with ketones, and many of them were partly hydrogenated to olefinic glycols. With the commercial availability of butynediol, dozens of patents and papers on the preparation of butenediol from butynediol soon appeared (137–152).

Much of the literature on *cis*-butenediol is clouded by inadequate analytical determination of the final product. Many products which have been described as pure *cis*-butenediol are actually (based on the physical constants reported) crude mixtures. The hydrogenation of butynediol is complex; Reppe reports butanediol, butenediol, 4-hydroxybutyraldehyde, 1-butanol, tetrahydrofuran, and furan (153). Romanet (154) describes the following composition for the product of partial hydrogenation of butynediol in ethanol with Raney nickel: 52% *cis*-butenediol, 14% *trans*-butenediol, 11% butanediol, 10% butynediol, 8.5% 2,5-dihydrofuran, and 1.5% 2-buten-1-ol.

PROPERTIES

Butenediol, as manufactured commercially in the United States, is predominantly the *cis* isomer. It is very soluble in water, methanol, ethanol, and acetone. It is difficultly soluble in benzene and other aromatic solvents.

Commercially available butenediol has a purity of 93–95%. Typical impurities include water, 2-butyne-1,4-diol, and 1,4-butanediol. Butenediol is shipped in steel containers, tank wagons, and tank cars.

Butenediol is stable at ordinary temperatures. At temperatures in excess of 165°C, butenediol dehydrates and polymerizes slowly. Some physical properties of butenediol are listed in Table 3.

The chemical properties of butenediol result from the olefinic group and the two primary terminal hydroxyl groups.

Table 3. Physical Properties of Butenediol

Property	Commercial ^a	Purified ^b
solidification point, °C	7.0	11.77
refractive index, n_D^{25}	1.475–1.477	1.4768–1.4773
specific gravity, 25/15°C	1.067–1.074	1.070
boiling point, °C		
760 mm Hg		234
100 mm Hg		177
20 mm Hg	142–147	
10 mm Hg		122
5 mm Hg		109
flash point, open cup, °F	263	
fire point, open cup, °F	260	
viscosity, cps		
20°C	22	
38°C	10.8	
99°C	2.5	

^a 95% minimum butenediol. ^b 98–99% *cis*-butenediol.

Reactions of the Double Bond. Butenediol readily takes part in Diels-Alder addition to dienes such as cyclopentadiene (155), anthracene (156), hexachlorocyclopentadiene (157), and 9,10-dihydroanthracene (158). The Diels-Alder reaction product of butenediol and cyclopentadiene (or halogen-substituted cyclopentadiene) can be further reacted with thionyl chloride to form the cyclic sulfite (159,160); with formaldehyde to form the cyclic formal (161); or cyclized via dehydration to form the tetrahydrophthalan derivative (162–164).

Butenediol adds halogens at the double bond to give dihalobutanediols (132, 165,166). The reaction product of butenediol and bromine, 2,3-dibromo-1,4-butanediol, is readily converted to butadiene dioxide by treatment with alkali (131,165,166).

Butenediol can be converted to the epoxide by treatment with hydrogen peroxide and an acid salt of a heavy metal peracid (167).

Oxidation of butenediol with hydrogen peroxide or with persulfates yields racemic erythritol (168,169); with hydrogen peroxide–acid mixture containing an oxygen carrier, 3,4-dihydroxytetrahydrofuran is obtained (170).

Butenediol may be copolymerized with vinyl esters to give low-molecular-weight polymers containing primary hydroxyl groups (171).

Reactions of the Hydroxyl Groups. Reaction of butenediol with monobasic acid halides or anhydrides yields esters such as the diacetate (172,173), the dibenzoate (132), and the methacrylate (174).

Polyesters are formed by reaction with dibasic acids such as sebacic acid (130), adipic acid (175), and maleic and fumaric acids (176).

Butenediol is readily dehydrated to 2,5-dihydrofuran in the presence of acid catalysts (177); when heated with catalytic amounts of cupric chloride, bimolecular condensation occurs to form 2,5-divinyl-1,4-dioxane (178). 2,5-Dihydrofuran is a source of α -amino- γ -hydroxyvaleric acid (177,179,180).

Butenediol also reacts with hydrogen chloride at 50°C to give 1,4-dichloro-2-butene in high yields; at lower temperatures it gives 4-chloro-2-buten-1-ol (181,182). Reaction with hydrogen bromide at 0–10°C gives 1,4-dibromo-2-butene (132). Treatment with nitric acid yields butenediol dinitrate (183). Condensation with styrene gives the bis(α -methylbenzyl) ether of butenediol (176). Reaction with hydrogen cyanide in the liquid phase at 60–80°C gives 1,4-dicyano-2-butene (184). With ammonia or primary amines, butenediol yields pyrroline or *N*-substituted pyrrolines (185). Butenediol reacts with acrylonitrile to form 3,3'-(2-butenylene-1,4-dioxy)di-propionitrile (186).

Butenediol, with a nickel catalyst, isomerizes to γ -hydroxybutyraldehyde (187).

Analysis. Butenediol is determined via bromination of the double bond.

HEALTH AND SAFETY FACTORS

Butenediol is a primary irritant but it is not a skin sensitizer. The liquid is harmful if swallowed. Care should be exercised to avoid breathing vapors. Adequate ventilation should be provided.

Acute oral toxicity: LD₅₀ = 1.25 ml/kg (white rats); 1.25–1.5 ml/kg (guinea pigs). Butenediol is in the same toxicity range as acetanilide, acetophenone, morpholine, and naphthalene acetic acid.

Butenediol presents no special handling problems. During cold weather the product should be stored at temperatures above 45°F for ease in handling.

MANUFACTURE

In the early production of butenediol in Germany, the catalyst was made from a paste of pure iron (from iron carbonyl) and butanol, coated on pumice granules of about 5-mm mesh. These were then heated in a furnace at 500°C in a stream of hydrogen (188,189). Raney iron and electrolytic iron were found to be equally satisfactory as catalysts. Various other catalysts tried, including partly poisoned nickel and cobalt, were unsatisfactory.

The reactor was a steam-jacketed vertical tube, 5 meters high and 12 centimeters in inner diameter, containing 50 liters of catalyst.

An approximately 34% aqueous butynediol solution was pumped at 15–25 liters per hour together with hydrogen into the top of the converter which was maintained at 200 atm pressure. The heat of reaction was controlled partly by means of the jacket and partly by recirculation of excess hydrogen.

The initial operating temperature was 50°C. As the catalyst deteriorated, over a period of 5–6 weeks, the temperature was progressively raised to 90°C. When the reactor was operated above 90°C, the yield suffered greatly.

The product was dehydrated and then distilled at reduced pressure. The yields,

calculated on butynediol input were—butenediol, 83%; butanediol, 10%; butynediol, 0–2% (recovered).

USES

Butenediol is used in the production of the Diels-Alder addition product with hexachlorocyclopentadiene (157). The resulting adduct is treated with thionyl chloride, giving a cyclic sulfite which is an effective insecticide, Thiodan (Niagara Chemicals Division, Food Machinery & Chemical Corp.) (159).

The diester of butenediol and bromoacetic acid, *cis*-1,4-bis(bromoacetoxy)-2-butene, is used as a fungicide, germicide, and slimicide in paper manufacture (186).

The addition of 0.05 to 1.5 grams of butenediol per liter of nickel salt to electrolytic plating solutions gives bright, dilute nickel plate. It is used in combination with sulfo-oxygen compounds such as naphthalenetrisulfonic acid (187).

Butenediol is used as a reducing agent for hexavalent chromium salts in the preparation of chrome tanning baths (190).

It is used as an intermediate in the preparation of butadiene diepoxide by reaction with bromine followed by dehydrohalogenation (131,132,163,165,166).

Polyurethane structural laminates from toluenediisocyanate and butenediol give high flexural strength and flexural modulus (191).

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SECONDARY AND TERTIARY ACETYLENIC AND ETHYLENIC ALCOHOLS AND GLYCOLS

In this article, the term "alcohols" will often be used to denote the monohydric alcohols, obtained by reaction of acetylene with one molecule of a carbonyl compound, as opposed to the glycols, obtained with two molecules of carbonyl compound.

In reactions of acetylene with formaldehyde (discussed previously) and with ketones (see p. 621), either one or two molecules of carbonyl compound may react with acetylene, according to the conditions, giving either monohydric alcohols or glycols. With aldehydes, owing to the ease of aldolization, it is sometimes difficult to isolate the secondary glycols from the reaction mix. Since aldolization is minimized in the case of sterically hindered aldehydes, some glycols are readily prepared in good yields. For example, the acetylenic glycol from isobutyraldehyde can be prepared readily in

good yields (1). However, since the glycols have been difficult to obtain, research on their chemistry has not been very extensive and they are not discussed in this article.

Secondary acetylenic alcohols.....	619
Tertiary acetylenic alcohols.....	621
Tertiary acetylenic glycols.....	625
Secondary and tertiary ethylenic alcohols and glycols.....	629
Bibliography.....	634

Secondary Acetylenic Alcohols

The secondary acetylenic alcohols are obtained by the reaction of acetylene with aldehydes (2-4).



PHYSICAL PROPERTIES

The lower secondary acetylenic alcohols (C₄ to C₁₀) are soluble in water, benzene, chlorinated solvents, Cellosolve, ethanol, low-boiling aliphatic hydrocarbons, and most ketones and esters. They are sparingly soluble in mineral oil and kerosene.

The best known members of this group are the following:

Name	Formula	Starting material
1-pentyn-3-ol	HC≡C—CHOHCH ₂ CH ₃	propionaldehyde
4-methyl-1-pentyn-3-ol	HC≡C—CHOHCH(CH ₃)CH ₃	isobutyraldehyde
1-hexyn-3-ol	HC≡C—CHOHCH ₂ CH ₂ CH ₃	butyraldehyde
4-ethyl-1-octyn-3-ol	HC≡C—CHOHCH(Et)CH ₂ CH ₂ CH ₂ CH ₃	2-ethylhexanal

Some physical properties of these alcohols are given in Table 1.

Table 1. Physical Properties of Some Acetylenic Alcohols

Property	1-Pentyn-3-ol	4-Methyl-1-pentyn-3-ol	1-Hexyn-3-ol	4-Ethyl-1-octyn-3-ol
appearance	clear, colorless liquid	clear, colorless liquid	light, yellow liquid	clear, pale yellow liquid
odor	piercing, resembling terpenes	like isopropyl alcohol-camphor mixture	musty, terpene-like	penetrating
boiling point, 760 mm Hg	125	131-132	142	197.2
freezing point, °C	-70 to -80	-43	-80	-45
specific gravity, 20/20°C	0.906	0.878	0.882	0.873
refractive index, n _D ²⁰	1.4322	1.4357	1.4350	1.4502
flash point, Tag open cup, °F		106		182

CHEMICAL PROPERTIES

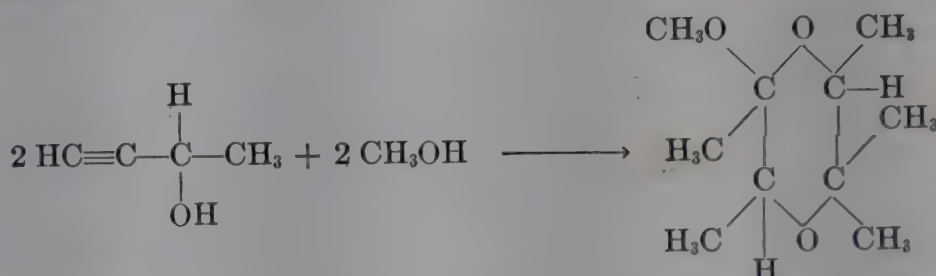
The chemistry of the secondary acetylenic alcohols has been given only the most cursory examination and the documentation which is presented in various reviews is extremely poor. Copenhaver and Bigelow present a table of reactions of 1-butyn-3-ol, the secondary acetylenic alcohol from acetaldehyde, which depicts the possibility of semihydrogenation to butenol, hydration to 2-hydroxy-3-butanone, and dehydration to vinylacetylene (5). However, no further documentation is given.

Esterification. Secondary acetylenic alcohols generally can be esterified in good yields by refluxing the alcohol with acid anhydrides (6-10). Esters may also be prepared by refluxing with acid halides and sulfonic acid halides in either the presence or absence of pyridine (9,10). Attempts to esterify 4-methyl-1-pentyn-3-ol by refluxing acetic acid in the presence of *p*-toluenesulfonic acid or sulfuric acid gave poor results (1). Esterification performed by refluxing the alcohol with excess acetic anhydride proceeds smoothly. Reaction with phthalic anhydride in the presence of pyridine yields only the monoester (11). Treatment of secondary acetylenic alcohols with carbamyl chloride in the presence of pyridine leads to the carbamate (12).

Hydrolysis. Secondary acetylenic alcohols are cleaved to acetylene and aldehyde when heated with 15% potassium hydroxide (7,8).

Hydration. Hydration of the triple bond in secondary acetylenic alcohols can be achieved by reaction with mercuric sulfate and sulfuric acid in an aqueous or an aqueous-methanol system (13). Use of a mercuric acetate-acetic acid-water system was not very successful.

Rearrangement. Concentrated sulfuric acid under gentle heating converts 4-methyl-1-pentyn-3-ol to mesityl oxide (4-methyl-3-penten-2-one) (14). Substituted dioxanes are formed from alcohols and secondary acetylenic alcohols in the presence of HgO , BF_3 etherate catalyst (15).



Semihydrogenation (triple bond to double bond). Semihydrogenation of secondary acetylenic alcohols occurs using 5% palladium on BaCO_3 or CaCO_3 at 30-55 psi and 30-60°C (1).

Ethoxylation. Ethylene oxide can be reacted with secondary acetylenic alcohols using a dimethyl aniline catalyst at temperatures of 55-150°C and 70-100 psi to obtain the monooxyethanol ether, $\text{HC}\equiv\text{C}-\text{CHROCH}_2\text{CH}_2\text{OH}$ (1).

Cyanoethylation. 1-Pentyn-3-ol or 1-hexyn-3-ol, when treated with acrylonitrile in the presence of 40% KOH, gives high yields of the cyanoethyl ether, $\text{HC}\equiv\text{C}-\text{CRO}-\text{CH}_2\text{CH}_2\text{CN}$ (16).

Oxidation. Secondary acetylenic alcohols can be oxidized, using CrO_3 and H_2SO_4 , to the corresponding acetylenic ketones. 1-Pentyn-3-ol leads to 1-pentyn-3-one and 1-hexyn-3-ol to 1-hexyn-3-one (6,17).

Glycol Formation. The ethynyl group of secondary acetylenic alcohols, like most ethynyl groups, can be oxidatively coupled to give in this case secondary diacetylenic glycols, $\text{HOHRC}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{CHROH}$. The reaction is performed using oxygen in an aqueous solution of the alcohol, with a catalyst mixture of cuprous chloride and ammonium chloride (18,19).

Halogenation. 1-Hexyn-3-ol when warmed with thionyl chloride, SOCl_2 , and pyridine gives good yields of 3-chloro-1-hexyne (20,21). 1-Pentyn-3-ol when treated with bromine in chloroform solution leads to 1,2-dibromo-1-penten-3-ol (22).

Dehydration. The secondary acetylenic alcohols can be dehydrated by passing over MgSO_4 at 270°C yielding ene ynes (23).

USES

Secondary alcohols have been found useful for inhibiting corrosion of ferrous metals in nonoxidizing acidic solutions (1,24).

Tertiary Acetylenic Alcohols

The best known of the tertiary acetylenic alcohols is $\text{HC}\equiv\text{C}-\text{C}(\text{CH}_3)\text{OHCH}_3$, obtained from the reaction of acetylene with acetone. It is correctly designated as 2-methyl-3-butyn-2-ol. (The “ol” group takes the lowest possible number; the “yn” is then given the lowest number available.) 2-Methyl-3-butyn-2-ol is known commercially simply as “methyl butynol,” and will be so referred to here.

PHYSICAL PROPERTIES

Methyl butynol is a clear colorless liquid with a pleasant fragrant odor. At room temperature it is miscible with water and the following solvents: acetone, benzene, carbon tetrachloride, Cellosolve, cyclohexanone, diethylene glycol, ethyl acetate, kerosene, methyl ethyl ketone, mineral spirits, monoethanolamine, neat’s-foot oil, petroleum ether (bp 60°C), soybean oil, and Stoddard solvent. It is immiscible with mineral oil (Nujol). Methyl butynol is an active solvent for cellulose acetate, cellulose acetate butyrate, low-molecular-weight epoxy resins, isocyanate resins, rosin-modified maleic resins, phenolic-type resins, polyacrylate resins, low-molecular-weight poly(vinyl acetate), poly(vinyl butyral) resins and shellac. Some of the physical properties of methyl butynol are given in Table 2.

Table 2. Physical Properties of Methyl Butynol

boiling point, °C, 760 mm Hg	104–104.5
freezing point, °C	2.6
specific gravity, 20/20°C	0.867
refractive index, n_D^{20}	1.4211
flash point, Tag open cup	25°C (77°F)
viscosity at 20°C, cps	3.79
surface tension at 25°C, dynes/cm	
bulk	23.8
5% by wt in H ₂ O	41.7
solubility in water, wt-%	miscible in all proportions
vapor pressure, mm Hg	
at 16°C	10
at 57°C	100
at 80°C	300
at 103.6°C	760

Methyl butynol forms azeotropes with various compounds, having the following boiling points: 28.4% water, 90.7°C; 96.2% 1,1,1-trichloroethane, 72.5–73.5°C; 44.6% toluene, 98.7–99.1°C; 89.5% trichloroethylene, 85.2°C.

Several other tertiary acetylenic alcohols are available: 3-methyl-1-pentyn-3-ol, $\text{HC}\equiv\text{C}-\text{C}(\text{CH}_3)\text{OHCH}_2\text{CH}_3$, obtained from methyl ethyl ketone; 3,5-dimethyl-1-hexyn-3-ol, $\text{HC}\equiv\text{C}(\text{CH}_3)\text{OHCH}_2\text{CH}(\text{CH}_3)_2$, obtained from methyl isobutyl ketone; 1-ethynylcyclohexan-1-ol, $\text{HC}\equiv\text{C}-\text{COHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$, obtained from cyclohexanone. Some of the physical properties of these alcohols are given in Table 3.

Table 3. Physical Properties of Other Tertiary Acetylenic Alcohols

Property	3-Methyl-1-pentyn-3-ol	3,5-Dimethyl-1-hexyn-3-ol	1-Ethynyl-cyclohexan-1-ol
odor	sweet, heavy	camphor	sweet
appearance	colorless liquid	colorless liquid	white, crystalline solid
boiling point, °C, 760 mm	121–122	150–151	180
freezing point, °C	–30.6	–68	30–31
refractive index, n_D^{20}	1.4318	1.4353	
specific gravity, 20/20°C	0.8721	0.8545	
flash point, Tag open cup, °F	101.3	134	
viscosity at 20°C			
surface tension at 25°C, dynes/cm			
bulk	23.8	23.8	
5% by wt in H ₂ O	34.1		
1% by wt in H ₂ O		32.4	42.8
solubility in water, wt-%, 20°C	9.9	1.2	2.5

CHEMICAL PROPERTIES

The reactive centers of the tertiary acetylenic alcohols are the acetylenic hydrogen, the triple bond, and the hydroxyl group. The tertiary hydroxyl group offers the main area of differentiation in that it possesses the normal degree of reactivity and ease of dehydration characteristic of tertiary compounds.

Reactions of the Hydroxyl Group. Tertiary acetylenic alcohols do not undergo simple esterification by direct reaction of the alcohol with aliphatic acids. The acetates are formed either by reflux with excess acetic anhydride and sodium acetate (25) or phosphoric acid (26), or by the reaction with ketene and sulfuric acid (27). Another method is ester exchange between the acetylenic alcohol and isopropenyl acetate in the presence of sulfuric acid (26,28). The stearate and benzoate esters are prepared by treatment with the acid chloride in the presence of pyridine (25,29). Refluxing with alkyl isocyanates gives the corresponding *N*-alkyl carbamates (30). Reaction of the acetylenic alcohols with phosgene and dry ammonia leads to the unsubstituted carbamate derivative (31–33).

Methyl butynol is dehydrated to isopropenylacetylene, $\text{HC}\equiv\text{C}-\text{C}(\text{CH}_3)=\text{CH}_2$; heating with 30% sulfuric acid will give a 90% yield (27). In general, any acidic medium will readily remove water from the tertiary acetylenic alcohol molecule. Etherification can be effected by dimethyl sulfate using a sodamide catalyst although the yields are low (34). Methyl butynol reacts with acrylonitrile to give fairly good yields of the cyanoethyl ether, $\text{HC}\equiv\text{C}-\text{C}(\text{CH}_3)_2\text{OCH}_2\text{CH}_2\text{CN}$ (35). Trichloroacetaldehyde when reacted with the hydroxy group of methyl butynol results in the trichlorohemiacetal, $\text{HC}\equiv\text{C}-\text{C}(\text{CH}_3)_2\text{OCHOHCCl}_3$ (36). Vinyl ethers result in the normal acetal (37,38).

Hydrochlorination using concentrated hydrochloric acid yields mainly 3-chloro-3-methyl-1-butyne when carried out in the presence of excess acid, calcium chloride, and hydroquinone, although varying amounts of 1-chloro-3-methyl-1,2-butadiene, 2-chloro-3-methyl-1,3-butadiene, and 2-methyl-1-buten-3-yne are also formed (39). Both ethylene and propylene oxides react to yield hydroxyalkyl ethers of methyl butynol in the presence of a mildly alkaline catalytic agent such as dimethylaniline (40,41).

Reaction with 50% hydrogen peroxide in the presence of sulfuric acid gives almost a quantitative reaction of the hydroperoxide (42).

Reactions of the Triple Bond. Acidic mercury salts in the presence of water act as catalysts to hydrate the triple bond in acetylenic alcohols to yield the corresponding hydroxy ketones ($\text{HC}\equiv\text{C}-$ to $\text{CH}_3\text{CO}-$). Sulfuric acid and mercuric sulfate (43) are usually used as the catalyst although mercuric oxide and sulfuric acid (44,45) or the mercuric salt of Dowex 50 (sulfonated polystyrene ion-exchange resin) (46) serve satisfactorily. A special type of hydration occurs when alcohol is substituted for water using a catalyst system composed of mercuric oxide, boron trifluoride, and trichloroacetic acid to yield the ketal, $\text{CH}_3\text{C}(\text{OR})_2\text{COH}(\text{CH}_3)_2$ (28,47). Ethylene glycol gives the cyclic ketal. When aniline is treated with methyl butynol in the presence of HgO and BF_3 , a reaction similar to hydration takes place with the formation of an anil, $\text{CH}_3\text{C}(=\text{NC}_6\text{H}_5)\text{COCH}(\text{CH}_3)_2$ (48).

The triple bond in acetylenic alcohols can be hydrogenated to yield either the ethylenic or the saturated analogs. Palladium-barium carbonate (26) is employed for semihydrogenation, whereas alkali-promoted Raney nickel at atmospheric pressure serves for preparing the saturated analog (25).

Aqueous potassium permanganate will oxidize methyl butynol to α -hydroxyisobutyric acid (49). Chlorination of methyl butynol can lead to a mixture of products, the principal one being 1,1,2,2-tetrachloro-3-methylbutan-3-ol, with some four others. The ratio of the latter product to the other four depends on the solvent employed (50,51). Bromination in chloroform principally yields the 1,2-dibromo ethylenic alcohol (52).

The acetylenic bond in methyl butynol is capable of reaction with nickel tetracarbonyl, $\text{Ni}(\text{CO})_4$, in two ways. When reacted in the presence of an alcohol such as butyl alcohol, and hydrogen chloride, the product is 5-butoxy-2-methyl-3-hydroxy-3-pentene (53). Cyclization to tris-(2,4,6- α -hydroxyisopropyl)benzene (54) takes place when the reaction is carried out in the presence of the triphenylphosphine complex of $\text{Ni}(\text{CO})_4$.

Two moles of sodium bisulfite will add to the triple bond of methyl butynol to give the disodium salt of 3-methyl-3-hydroxy-1,2-butanedisulfonic acid (30).

Reactions of the Acetylenic Hydrogen. Acetylenic alcohols can be oxidatively coupled by removal of the acetylenic hydrogen to form diyne diols, $\text{RR}'\text{HOC}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{COHRR}'$. The reaction is quantitative in aqueous solution using oxygen as the coupling agent in the presence of a mixture of ammonium chloride and cuprous chloride catalyst (55).

The acetylenic hydrogen in acetylenic alcohols can be further reacted in the presence of potassium hydroxide and ether with ketone containing moieties such as 3-methyl-3-hydroxy-2-butanone to obtain in the case of methyl butynol the acetylenic triol, 2,3,6-trimethyl-2,3,6-trihydroxy-4-heptyne, in good yields (56,57). Replacement of the acetylenic hydrogen with formaldehyde to give the mixed primary-tertiary acetylenic glycol, $\text{H}_2(\text{HO})\text{C}-\text{C}\equiv\text{C}-\text{C}(\text{OH})\text{RR}'$, can be effected using paraformaldehyde and ethylmagnesium bromide (51). The use of trimethylchlorosilane under the same conditions with methyl butynol gives trimethyl-(3-methyl-3-hydroxy-1-butynyl)-silane, $(\text{CH}_3)_3\text{Si}-\text{C}\equiv\text{C}-\text{C}(\text{CH}_3)_2\text{OH}$ (58).

Reaction of acetylenic alcohols with strong aqueous solutions of hypohalites allows

easy replacement of the acetylenic hydrogen yielding the 1-halo acetylenic alcohols. The reaction is known for chlorine, bromine, and iodine (52,59,60).

The acetylenic hydrogen is acidic enough in character to be replaceable by metals under certain conditions. Methyl butynol in liquid ammonia reacts with sodamide to give the sodio derivative which can be treated with carbon dioxide to yield a carboxy acetylenic alcohol (25).

Reactions of the Hydroxyl Group and Triple Bond. Reaction of acetylenic alcohols with organic acids in the presence of the mercuric ion and boron trifluoride simultaneously hydrates the triple bond and esterifies the hydroxyl group (61–64). Methyl butynol undergoes a rearrangement (modified Rupe reaction) when treated with formic acid to yield an unsaturated aldehyde, 3-methyl-2-butenal (65–67). A substituted allene, 3-methyl-1,2-butadiene, is obtained when methyl butynol is reacted with concentrated hydrochloric acid and lithium aluminum hydride (68). The reaction of methyl butynol with hydrogen bromide yields a mixture of four products, the main ones of which are 1,3-dibromo-3-methylbutane and 1,2,3-tribromo-3-methylbutane (44).

Stability. The acetylenic alcohols are flammable liquids (for example, methyl butynol has a 77°F flash point) and the precautions normally observed in handling such materials should be used. They are quite stable at room temperatures and may be distilled without decomposition at atmospheric pressure. The pH of the still charge should be essentially 7, since, under acid conditions and heat, dehydration to more volatile ethylenic-acetylenic hydrocarbons will occur, whereas, under basic conditions, degradation to acetylene and the ketone takes place.

Materials of Construction. The acetylenic alcohols may be stored in mild-steel drums and tanks, and this material is suitable for reaction vessels, pumps, and piping. Glass, Monel, stainless steel, aluminum, zinc, low copper brass (less than 60% copper), cast iron, and galvanized steel are also suitable. Acetylene is known to react with copper to form explosive acetylides and, since acetylenic alcohols are monosubstituted acetylenes, copper should be avoided in its handling. For the same reasons, silver is not recommended for use.

Method of Analysis. The sample is weighed into an excess of aqueous neutral silver nitrate solution. Using a methyl purple indicator, the mixture is titrated to the green-color end point of the indicator with 0.1*N* aqueous sodium hydroxide. The reaction actually is a titration of nitric acid liberated when the silver replaces the ethynyl hydrogen.

Toxicity. The presence of the tertiary hydroxyl group in the acetylenic alcohols renders them relatively nontoxic when compared with similar structures not containing the tertiary configuration (69). Oral toxicity (mice): methyl butynol, 2.2 g/kg; methyl pentynol 0.7 g/kg.

USES

The acetylenic alcohols are useful reactive intermediates with application in the pharmaceutical, perfume, plastic, rubber, and specialty chemical industries. Direct applications include their use as solvents and solvent modifiers, acid inhibitors, viscosity reducers and stabilizers, electroplating brighteners, and halogenated solvent stabilizers.

Methyl butynol is a typical example of a member of this class of acetylenic alcohols. Methyl butynol is effective in inhibiting the attack of aqueous mineral acids at elevated temperatures on mild steel, aluminum, and zinc. The concentration range is normally 0.1–0.5%.

Methyl butynol at low concentrations (based on acid content) effectively prevents the infusion of hydrogen into steel during acid immersion, the metal thereby retaining its original ductility.

Effective use of methyl butynol in conjunction with water soluble sulfo-oxygen compounds has been established in electroplating processes for bright nickel plating (35).

Methyl butynol has a definite retarding or inhibiting effect on the degradation of halogenated solvents (54). The use of methyl butynol with one or more inhibiting materials such as thymol, di-*tert*-butyl-*p*-cresol, epichlorohydrin, butylene oxide, aliphatic and heterocyclic amines, and dioxane gives synergistic halogenated solvent stabilization (70). Concentrations of 0.005–0.3% have been suggested for this use.

Methyl butynol is effective as a viscosity reducer and antigelling agent in compounding flexographic (aniline) inks, at about 2% concentration, and in the formulation of rubber cement (71).

Methyl butynol and certain other acetylenic monohydric alcohols exhibit varying degrees of hypnotic activity (36). It is also claimed that the acetylenic bromide and chloride (Br or Cl replacing H on the 1-carbon atom) of methyl butynol have increased hypnotic activity over methyl butynol (72).

Methyl butynol has also been utilized as an intermediate in the synthesis of important perfume materials (73).

Tertiary Acetylenic Glycols

The best known of the tertiary acetylenic glycols are found in Table 4.

Table 4. Tertiary Acetylenic Glycols

Name	Formula	Starting Material
2,5-dimethyl-3-hexyne-2,5-diol	$(\text{CH}_3)_2\text{C}(\text{OH})\text{—C}\equiv\text{C—C}(\text{OH})\text{—}(\text{CH}_3)_2$	acetone
3,6-dimethyl-4-octyne-3,6-diol	$(\text{C}_2\text{H}_5)(\text{CH}_3)\text{C}(\text{OH})\text{—C}\equiv\text{C—C—}(\text{OH})(\text{CH}_3)(\text{C}_2\text{H}_5)$	methyl ethyl ketone
4,7-dimethyl-5-decyne-4,7-diol	$(n\text{—C}_3\text{H}_7)(\text{CH}_3)\text{C}(\text{OH})\text{—C}\equiv\text{C—C—}(\text{OH})(\text{CH}_3)(n\text{—C}_3\text{H}_7)$	methyl <i>n</i> -propyl ketone
2,4,7,9-tetramethyl-5-decyne-4,7-diol	$(iso\text{—C}_4\text{H}_9)(\text{CH}_3)\text{C}(\text{OH})\text{—C}\equiv\text{C—C}(\text{OH})(\text{CH}_3)(iso\text{—C}_4\text{H}_9)$	methyl isobutyl ketone

PHYSICAL PROPERTIES

The tertiary acetylenic glycols are white solids varying in consistency from soft waxy solids to crystalline materials. Some of their physical properties are given in Table 5.

CHEMICAL PROPERTIES

The molecular structure of the tertiary acetylenic glycols is such that the acetylenic bond imparts a linear rigidity to the four central carbon atoms. This rigidity, the ditertiary configuration, and the 1–4 spacing of the hydroxyl carbons all contribute to the properties of these chemicals. In certain of the molecules there has been observed surface-active properties owing to a balance between the hydrophobic hydrocarbon segments, on the one hand, and the hydrophilic acetylenic linkage and hydroxyl groups,

Table 5. Physical Properties of Some Tertiary Acetylenic Glycols

Property	2,5-Dimethyl-3-hexyne-2,5-diol	3,6-Dimethyl-4-octyne-3,6-diol	4,7-Dimethyl-5-decyne-4,7-diol	2,4,7,9-Tetramethyl-5-decyne-4,7-diol
appearance	white, crystalline	white, crystalline	white powder	white, waxy
boiling point, °C	205-206	222	253	260
melting point, °C	96-97	48-50	61-63	37-38
surface tension, dynes/cm (25°C, 0.1% in water)	60.9	55.3	51.1	45.1
solubility, ^a				
water, wt-%, 20°C	27.0	10.5	1.3	0.12
acetone	vs	vs	vs	vs
benzene	ss	vs	s	s
carbon tetrachloride	ss	vs	vs	vs
Cellosolve	vs	vs	s	vs
ethylene glycol, wt-%	vs	vs	vs	50
ethylene acetate	vs	vs	vs	vs
methyl ethyl ketone	vs	vs	vs	i
mineral oil	i	i	i	i
petroleum ether (bp, 50°C)	ss	s	s	s
Stoddard solvent	i	i	i	s

^a vs, very soluble; s, soluble; ss, slightly soluble; i, insoluble.

on the other. The high degree of unsaturation also contributes to the thermal stability of the compounds.

Esterification. Refluxing these acetylenic glycols with an excess of acetic anhydride in the presence of sodium acetate gives quantitative yields of the diester. Isopropenyl acetate also gives the diester by ester exchange in high yields. Using the acid chlorides and pyridine, it has been possible to prepare oleates, mono- and distearates, and dipelargonates (74).

It is possible to prepare an ethylenic monoacetate by treatment with acetic anhydride and mercuric acetate (75).

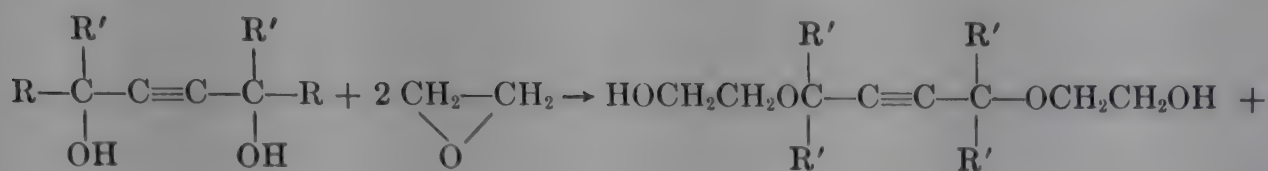


Attempted esterification using formic acid (76) leads to $\text{RR}'\text{C}=\text{CHCOC}(\text{OH})\text{RR}'$ and $\text{RR}'\text{CHCOCOCHRR}'$.

Etherification. The tertiary glycols react with lower molecular weight alcohols to form the mono- and diethers in good yields when sulfuric acid is employed as the catalyst (77).

Dehydration. The tertiary hydroxyl groups in the acetylene glycol molecule dehydrate readily to give the diene-yne series in the presence of aniline catalysts. The dehydration of 2,5-dimethyl-3-hexyne-2,5-diol yields diisopropenylacetylene, $\text{CH}_2=\text{C}(\text{CH}_3)-\text{C}\equiv\text{C}-\text{C}(\text{CH}_3)=\text{CH}_2$, when heated with *p*-toluenesulfonic acid (78).

Hydroxylation. It is possible to react the hydroxyl groups of the tertiary acetylenic glycols with cyclic oxides to obtain the corresponding hydroxy ethers. Weakly alkaline catalysts are generally used since the parent compound is subject to decomposition by strong bases. For example, using *N*-dimethylaniline as catalyst, the following reaction can be effected in a 71% yield (79).



polycondensation products

Cyanoethylation. It is possible in the presence of a basic catalyst, such as sodium methoxide, to react the tertiary acetylenic glycols with acrylonitrile resulting in the cyanoethylation of the hydroxyl groups. The reaction proceeds in a somewhat step-wise fashion so that both the mononitrile ether ($-\text{OH} \rightarrow -\text{OCH}_2\text{CH}_2\text{CN}$, 19% yield) and the dinitrile ether (48.7% yield) are formed (80).

Reduction. Reduction of the tertiary acetylenic glycols can lead to three different products—ethylenic glycols, saturated glycols, and saturated alcohols.

The ethylenic glycols, $\text{RR}'\text{C}(\text{OH})-\text{CH}=\text{CH}-\text{C}(\text{OH})\text{RR}'$, are formed by hydrogenation at moderate pressures with selected catalysts, such as Raney nickel or palladium metal on charcoal (81,82). Usually the *cis* isomer is formed almost exclusively. 2,5-Dimethyl-3-hexene-2,5-diol is a solid, but the higher ethylenic glycols are often viscous liquids. Hydrogenolysis is a side reaction of varying importance. The use of higher pressures (above 50 lb) with palladium or platinum catalysts leads to the saturated glycols (81,82). 2,5-Dimethylhexane-2,5-diol is a white crystalline solid; 3,6-dimethyloctane-3,6-diol is a viscous liquid that can be crystallized under certain conditions. The higher glycols are viscous liquids.

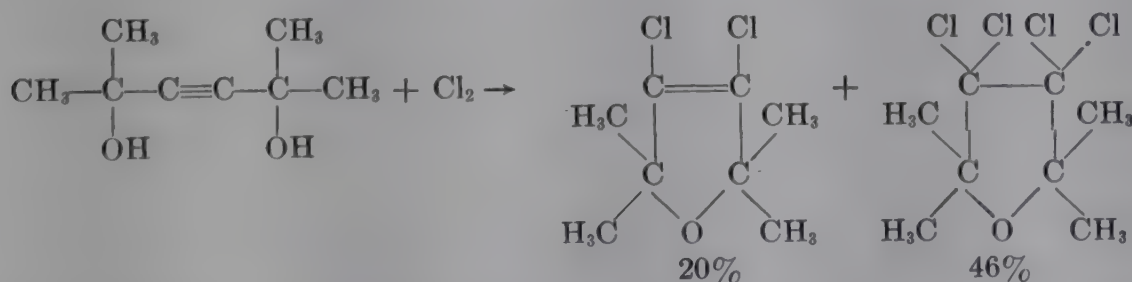
Hydrogenation of the acetylenic glycols under moderately high pressures and temperatures using nickel catalysts leads first to hydrogenation and then hydrogenolysis, one of the hydroxyls being reduced to hydrogen, giving a saturated monohydric alcohol. For example, 2,5-dimethyl-3-hexyne-2,5-diol will give 2,5-dimethylhexan-2-ol as the product (74,83).

Oxidation. The acetylenic bond in the tertiary acetylenic glycols can be cleaved using ozone in an aqueous system to give α -hydroxy acids (84,85). For example, 2,5-dimethyl-3-hexyne-2,5-diol leads to a α -hydroxyisobutyric acid $(\text{CH}_3)_2\text{C}(\text{OH})\text{COOH}$.

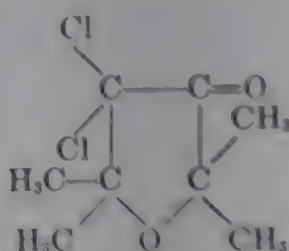
Oxidation using permanganate on the diester of the acetylenic glycol gives a diketone ($-\text{C}\equiv\text{C}-$ to $-\text{COCO}-$) (86).

It is possible to prepare the dihydroperoxides of the acetylenic glycols using sulfuric acid and hydrogen peroxide (87). These are stable solid compounds and can be handled safely under normal conditions.

Halogenation. The results of the halogenation of the tertiary acetylenic glycols are strongly affected by the solvent employed in the reaction. Cyclization usually takes place with the formation of more than one product. Using carbon tetrachloride or chloroform the following reaction takes place with chlorine.

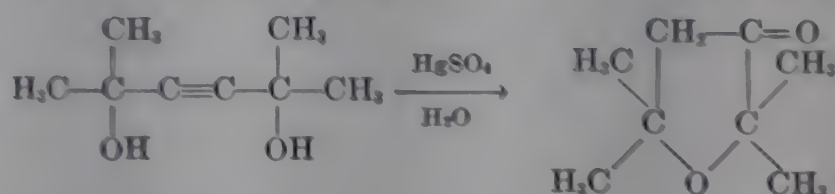


The use of bromine or iodine leads to high yields of the dihalo compound (88). In an aqueous medium, hydration of the acetylenic bond occurs (74), with the formation of



Hydrohalogenation. The reaction of tertiary acetylenic glycols with hydrogen halides gives a mixture of products (89), including $RR'XC\equiv C-CXRR'$ and $RR'C=CX-CX=CRR'$.

Hydration. The tertiary acetylenic glycols (but not their diesters) cyclize to 2,2,5,5-tetrasubstituted tetrahydrofuranones when subjected to hydration using the normal mercuric sulfate–water catalyst system. The reaction is as follows (74,83):



These tetrahydrofuranones are fragrant, high-boiling liquids.

Stability. The tertiary acetylenic glycols are solids varying from materials that are white and crystalline to those that are soft and waxy. They are stable under neutral conditions despite the presence of a triple bond and are no more combustible than any organic compound of comparable physical properties. Their high degree of stability is evidenced by the fact that they can be distilled at atmospheric pressure without decomposition. As with the alcohols, it is desirable that the pH of the still charge be maintained at 7 since under basic conditions with heat, degradation to ketones and acetylene (for acetylenic alcohols) can take place. In the presence of heat and acidic conditions, dehydration occurs with the formation of diene–ynes.

Materials of Construction. The acetylenic glycols may be stored in mild-steel drums and tanks. Glass, Monel, stainless steel, aluminum, zinc, cast iron, and galvanized steel are also suitable. Although the triple bond does not contain a free ethynyl hydrogen to react with such metals as copper and silver to form explosive acetylides, it is desirable to avoid their use.

Method of Analysis. Analysis is made by acetylating the glycol with excess acetic anhydride in the presence of sodium acetate by refluxing together for several hours. Hydrolysis of the unreacted acetic anhydride followed by titration enables the consumption of acetic anhydride to be calculated and interpreted in terms of percent hydroxyl group (87,90).

Toxicity. The tertiary acetylenic glycols as a class appear to be relatively non-toxic materials with respect to oral ingestion or surface contact. “Dimethyl decynediol” has an LD_{50} (for rats) of 4.7 g/kg and “tetramethyl decynediol” has a value of 4.6 g/kg. No evidence of skin irritation has been noted with the handling of the products during production or laboratory work. Bar soaps containing up to 5% of either “dimethyl decynediol” or “tetramethyl decynediol” have been used for several days for bathing without causing skin irritancy.

“Dimethyl octynediol” has been tested for oral toxicity, inhalation exposure, and skin absorption for the purpose of establishing label requirements in accordance with the requirements of the Interstate Commerce Commission. No evidence of toxicity was found.

USES

Like the tertiary acetylenic alcohols, the tertiary acetylenic glycols have also been utilized as reactive intermediates to form products for various fields of applications. The distinctive features of these glycols are the acetylenic bond, the ditertiary hydroxyl groups, and the 1-4 spacing of the hydroxyl carbons. Due to the substituted groups on the adjacent carbons, the acetylenic bond is not so reactive as a terminal ethynyl group. The acetylenic bond imparts a linear rigidity to the four central carbon atoms, and also contributes to the thermal stability and reactivity of the hydroxyl groups, which esterify more readily than in saturated tertiary glycols. The presence of the acetylenic bond gives a higher surface activity than that of saturated ditertiary structures. Various applications have included their usage as coupling agents in the formulation of cutting oils, drycleaning formulations, cosmetic preparations, and textile and paper finishes, as pigment dispersing agents in aqueous and non-aqueous systems, as surfactants in nonfoaming and low-foam detergent formulations, emulsifying agents, and antifoaming agents, as froth flotation agents, viscosity reduction additives in vinyl chloride plastisols and in flexographic inks and other aqueous gum systems, corrosion inhibitors, etc. Antigellation properties have also been demonstrated in aniline inks and zein solutions.

Secondary and Tertiary Ethylenic Alcohols and Glycols

SECONDARY ETHYLENIC ALCOHOLS

The secondary acetylenic alcohols can be semihydrogenated to the corresponding ethylenic alcohols using a catalyst of 5% palladium on charcoal. At pressures of 50 lb/psig at temperatures of 20-30°C the hydrogenation rate is extremely slow and it is advisable to use temperatures of 50-60°C. An inert hydrocarbon solvent is also useful. Since hydrogenation under these conditions is not selective, that is, the reaction can proceed to the next stage of hydrogenation (the saturated alcohol), it is advisable to measure the hydrogen and to use only the quantitative amount. Some of the ethylenic alcohols prepared in this manner are listed in Table 6 along with some of their physical properties.

Table 6. Physical Properties of Some Secondary Ethylenic Alcohols

Alcohol	Bp, °C, 760 mm Hg	Refractive index, n_D^{20}
1-penten-3-ol	66-68 ^a	
4-ethyl-1-octen-3-ol	62-63 ^b	
1-buten-3-ol	106-107	1.4260
1-hexen-3-ol	140-141	1.4329
4-methyl-1-penten-3-ol	131-133	1.4359

^a At 100 mm Hg. ^b At 2 mm Hg.

A study has been made of the rearrangement of secondary alcohols $RCH(OH)-CH=CH_2$ to the isomeric primary alcohols $RCH=CHCH_2OH$ by treatment of the initial alcohol with acetic anhydride containing trichloroacetic acid which produces an acetate ester of the isomeric primary alcohol (91-96).

However, the reaction is not so straightforward as in the case of the tertiary ethyl-

enic alcohols with the result that the ratio of primary ester to secondary ester in the product is about 2:1.

TERTIARY ETHYLENIC ALCOHOLS

Preparation by Semihydrogenation. The semihydrogenation of tertiary acetylenic alcohols is summarized in A. W. Johnson's book (97) and in a review article by Campbell and Eby (98). A variety of catalysts have been employed for the purpose of semihydrogenation including palladium (99–110), nickel (109,111–118), iron (119, 120), and platinum (121–123). Most workers including Raphael (124) have come to the conclusion that palladium catalysts on one of a variety of supports is the preferred catalyst to obtain high yields of the ethylenic carbinols. Platinum is too active a catalyst and causes the reduction to proceed simultaneously to the saturated alcohol. Lindlar (125,126) has developed a palladium catalyst which is inactivated with lead acetate and which is claimed to be selective in reducing the triple bond to the double bond. Recently Hennion and coworkers (127) claimed that very small amounts of palladium (5%) on barium carbonate is a selective semihydrogenation catalyst for tertiary ethynyl carbinols. Laboratory experience has not supported this result.

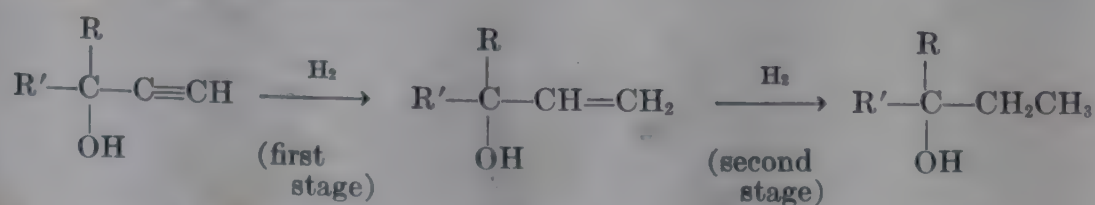
If palladium on barium carbonate is carefully used as the catalyst, 3-methyl-1-buten-3-ol will yield a crude ethylenic derivative of 95% purity. Other tertiary alcohols give inferior purities with this catalyst. The best general method for most acetylenic alcohols is palladium on either charcoal or barium carbonate in the presence of small amounts of KOH, NaOH, or triethyl amine (weight ratio of base to catalyst varies between 1:1 to 1:2) (128). The 95% grade crude can be upgraded to 98–99% by careful fractional distillation. The tertiary ethylenic alcohols which have been prepared are listed in Table 7 along with some of their physical properties.

Table 7. Physical Properties of Tertiary Ethylenic Alcohols

Alcohol	Bp, °C, 760 mm Hg	Refractive index, n_D^{20}
3-methyl-1-buten-3-ol	96–98	1.4166
3-methyl-1-penten-3-ol	115–116	1.4287
3,5-dimethyl-1-hexen-3-ol	146–148	1.4340
3-ethyl-5-methyl-1-hepten-3-ol	183–185	1.4441
3-methyl-1-nonen-3-ol	83–84 ^a	1.4422
1-vinylcyclohexan-1-ol	181	1.4769
3-ethyl-5-methyl-1-hepten-3-ol	94 ^b	1.4384
3-phenyl-1-buten-3-ol	84 ^c	1.5339

^a At 10 mm Hg. ^b At 25 mm Hg. ^c At 4 mm Hg.

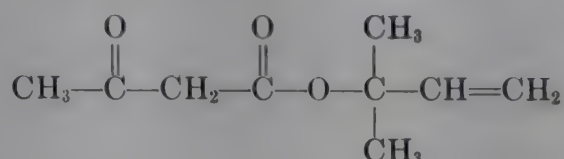
The hydrogenation of tertiary acetylenic carbinols can be represented, in general, as proceeding through two stages.



Unlike the related 1,4-acetylenic glycols, side reactions due to hydrogenolysis are insignificant.

Chemical reduction techniques can also be successfully employed to reduce acetylenic carbinols to the ethylenic analogs. Rupe (129) and Taylor and Shenk (130) have described procedures with fair yields using a zinc-copper couple. Other workers have used nascent hydrogen produced by a variety of procedures (109,131,132). An alternative is the reduction of acetylenic carbinols by sodium in liquid ammonia (98).

Esterification. The tertiary ethylenic alcohols can be esterified using procedures commonly used for tertiary alcohols. These include reactions with acetic anhydride with sodium acetate (133), ketene (134), and diketene (135). The latter product,



on further heating results in loss of CO_2 and a simultaneous anionotropic rearrangement to give 2-methyl-2-hepten-6-one which can be converted to citral, geraniol, or pseudonone.

Hydrogen Halide Addition. HCl can be added to the unsaturated group in the ethylenic alcohols to yield two isomers, 1-chloro-3-methyl-2-butene (64%) and 3-methyl-3-chlorobutene-1 (20%), (136). The original tertiary alcohol is primarily formed on hydrolysis. The reaction with bromine in carbon tetrachloride yields the 1,2-dibromo-3-hydroxy-3-methylbutane in an 85% yield (137).

Cyanoethylation. The ethylenic alcohols can be cyanoethylated using acrylonitrile in the presence of sodium to give the monocyanoethyl ether in 55% yield (138).

Dehydration. The ethylenic carbinols can also be dehydrated in good yields in the vapor phase over alumina at $290\text{--}300^\circ\text{C}$ (139) to yield terminal dienes. Alternatively the dienes can be prepared by refluxing the alcohol with ethyl benzene in the presence of aniline hydrobromide to give a high yield (140).

The dehydration of ethylenic alcohols leads to either simple or substituted butadienes depending on the starting materials which can be reacted with maleic anhydride to make the normal Diels-Alder adducts (141-145).

Oxidation. The ethylenic tertiary carbinols are not affected by reflux with the Oppenauer reagent under normal conditions. The oxidation of 3-methylbutenol to 3-methyl-1,2,3-butanetriol by the action of potassium chlorate and osmium tetroxide has been claimed by Bayer and Company (146). Ozonolysis at 15°C splits the double bond yielding a small amount of α -hydroxy-isobutyric acid and a large quantity of formic acid (147).

A series of reactions have been developed by Lespieau and his coworkers to convert acetylenic derivatives to their ethylenic analogs and to yield by further oxidation a variety of pentahydric and hexahydric sugar alcohols, including adonitol, arabitol, dulcitol, and allodulcitol (148-164).

Anionotropic Rearrangement. The tertiary ethylenic alcohols undergo a rearrangement in the presence of acid reagents to give α,β -unsaturated primary alcohols in a 35-50% yield (92,165).



This is a typical allylic rearrangement of the three-carbon system and considerable research has been carried on for this special type of reaction. The factors which generally influence the reaction are the nature of the migratory group and the acid strength of

its hydrogen derivative, the dielectric constant of the solvent medium, and the capacity of the residual part of the chain to supply electrons.

The reaction can be carried out in the presence of phosphorus tribromide in pyridine. Potassium acetate (166–170), phosphorus pentachloride (171), trichloroacetic acid (91,166,167), and acetic anhydride (91,168,171,172) have also been used.

Recently, a method, using acidic ion-exchange resins as a catalyst for the rearrangement to the primary alcohol, has been reported to give good yields and conversions (173).

SECONDARY AND TERTIARY ETHYLENIC GLYCOLS

This section discusses the unsaturated 1,4 secondary and tertiary ethylenic glycols of the following structure: $RR'COHCH=CHCRR'OH$, where R' in secondary = H, and R' in tertiary = alkyl, cycloalkyl, or aromatic group.

Preparation. As in the hydrogenation of the acetylenic monoalcohols the hydrogenation of the glycols will not stop spontaneously at the ethylenic stage and must be stopped artificially unless a saturated glycol is desired. Unlike the hydrogenation of the alcohols, the hydrogenation mechanism and operating conditions are considerably more complicated. In neutral solution hydrogenolysis takes place readily and leads to a saturated alcohol with the same number of carbon atoms. Cyclization to tetrahydrofuran derivatives takes place only if the hydrogenation is carried out in acid media. Campbell and Campbell have published a good review of the hydrogenation of acetylenic glycols (174).

Useful solvents for the hydrogenation are methyl and ethyl alcohols, ethyl acetate, and for certain special cases, water or ether. Higher alcohols, acetone, etc., are far too slow (175). As the radicals R' and R are increased in size and molecular weight, the rate of hydrogenation decreases, other conditions being equal. When certain catalysts such as palladium or platinum are used and the volume of hydrogen absorbed is plotted against the time, there is a distinct break in the curve at a point which roughly corresponds to the formation of the olefinic glycols. This is quite characteristic of the entire series, but it is still necessary to stop the reaction manually after the theoretical volume of hydrogen has been absorbed.

Considerable amount of research has been carried out on the use of specific catalysts. Palladium and platinum have been suspended on a wide variety of supports, such as carbon black, starch, and a series of inorganic materials. Each of these is supposed to have special characteristics but in general no variation in the product has been noticed. Since a less active catalyst than normal is desired to stop at the olefinic stage, it has been common practice to use partially poisoned catalysts (176,177). Nickel (176,178–180), cobalt (177,178), iron (181,182), and copper chromite catalysts (177) have been suggested.

The best method for selective hydrogenation involves the solution of the acetylenic glycol in solvent at 65°C in the presence of a trace of powdered potassium hydroxide (0.025–0.05 g per 0.5 mole of diol) using palladium on charcoal as the catalyst at 30–55 psig (183).

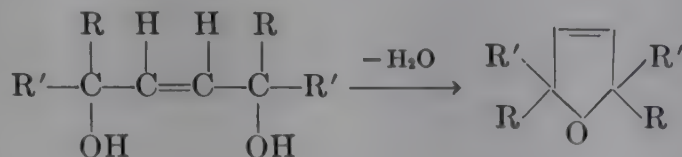
Noncatalytic methods of reduction, such as treatment with zinc in alkaline solution, have also been suggested (184).

Reactions. The ethylenic glycols $HOCRR'CH=CHCRR'OH$ can exist in two geometrically isomeric forms, *cis* and *trans*. When R is not the same as R' there are also stereoisomeric forms, for the two asymmetrically substituted carbon atoms can be

both dextro, or both levo, or the compound can be meso. This gives a total of six theoretically possible isomers.

In most cases it is possible to separate the cis and trans forms, although usually the proportion of the trans isomer is small and runs in the general area of about 10% of the whole (185–188). There is some reason to believe that the rate of hydrogenation and the nature of the catalyst determine the relative amounts of the cis and trans forms (189–194).

Dehydration of the Ethylenic Glycols. The ethylenic glycols can be dehydrated to yield dihydrofurans of the following type.



As would be expected the cis isomers naturally dehydrate much more readily than the trans isomers. Dehydration occurs readily in dilute acid solutions even at room temperature with more rapid reaction at elevated temperatures (195–199). The dehydration occurs not only with dilute mineral acids, but with any acidic agent—acid salts, acetic anhydride, phosphorus tribromide in pyridine, etc. Dehydration can also be performed catalytically at elevated temperatures over alumina (200,201).

Under special conditions it is possible for dehydration to take place in such a way that a normal conjugated triene is produced. This depends not only on reaction conditions but on structure. For example, the olefinic glycols resulting from phenylacetaldehyde and acetylene and from methyl ethyl ketone and acetylene followed by semihydrogenation can be dehydrated to the corresponding trienes. In the latter case the resulting compound is the acyclic terpene, allo-ocimene (202–204).

Hydroxylation. The ethylenic glycols can be hydroxylated at the double bond with hydrogen peroxide in the presence of catalysts, especially osmium tetroxide (205, 206) at a pH of 3.5 to 4 to give the expected tetrahydric alcohol (204).

Hydrohalide Addition. With hypochlorous acids the ethylenic glycols yield the normal chlorotriols. These compounds when subsequently subjected to hydrolysis give the normal tetrols (207).

Analysis. The 1,4-ethylenic glycols can be determined by the addition of bromine dissolved in methanol and catalyzed by the presence of aqueous hydrochloric acid. The assay can be made within 3 minutes and the end point does not change even after 10 minutes (208).

USES

None of the ethylenic alcohols and glycols mentioned above are at present in commercial production. Methyl butenol, 2,5-dimethyl-3-hexene-2,5-diol, and 3,6-dimethyl-4-octene-3,6-diol are offered by Air Reduction Chemical & Carbide Company in development quantities. The price for methyl butenol in 1961 was 90¢/lb, and the glycols were somewhat higher. If substantial uses are developed, there is no doubt that these prices could be markedly reduced. Methyl butenol is being used as a raw material for perfumes, vitamins, food colors, flavoring agents, and pharmaceuticals. It is also a source of pure isoprene. The ethylenic glycols are of interest as resin intermediates and as raw materials for the preparation of polymerization catalysts.

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M. W. LEEDS

Air Reduction Company, Inc.

ALDEHYDE RESINS. See Acetal resins.

ALDEHYDES

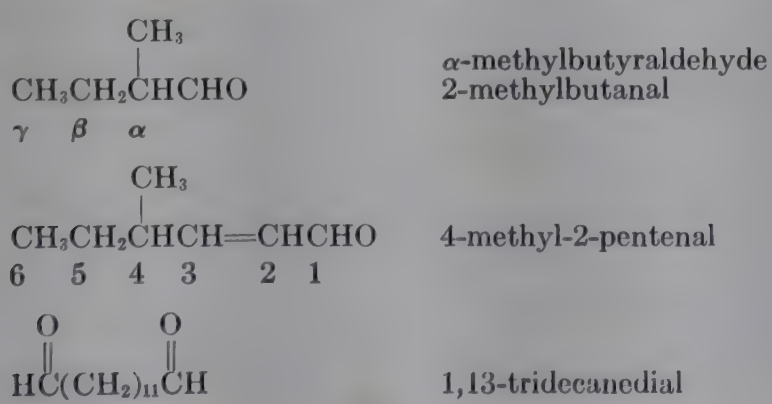
Aldehydes are organic compounds containing a carbonyl group attached to a terminal carbon atom; they may be represented by the general formula
$$\text{R}-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\text{H}.$$
 In formaldehyde, the simplest member of the class, R is hydrogen; for all other aldehydes R represents a hydrocarbon radical. Ketones (qv) $\text{R}-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\text{R}'$ are distinguished from aldehydes by having the carbonyl group attached to a nonterminal carbon atom. Aldehydes of industrial importance are discussed either under their own names (as Acetaldehyde or Benzaldehyde) or under the name of the corresponding acid (as Cinnamic Acid and cinnamaldehyde). See also Phenolic aldehydes.

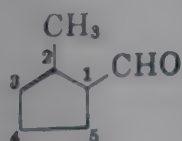
Nomenclature

The nomenclature of aldehydes corresponds closely to that of the related acids (see Acids, carboxylic). The three principal methods are the following:

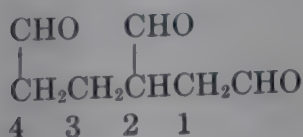
1. The common name method, in which aldehydes are named by dropping “-ic (or -oic) acid” from the common names of the corresponding carboxylic acids and adding “-aldehyde.”
2. The Geneva, or IUPAC system, according to which the names of aldehydes are formed by dropping the final “e” and adding “-al” to the names of the parent hydrocarbons. Where two aldehyde groups are present, the suffix “-dial” is added to the full hydrocarbon name. The Geneva system is employed for naming saturated and unsaturated aldehydes related to acids which do not have common names.
3. The carboxylic system, in which “-carboxaldehyde” is used similarly to “-carboxylic acid” in the case of acids. This method is used for aldehydes of many cyclic compounds and for aliphatic aldehydes which do not have convenient names under the Geneva system.

In addition, for compounds containing certain other functional groups in addition to the aldehyde substituent, the latter is denoted by the prefix “formyl.” The positions of substituents in aldehydes are designated either by numerals or Greek letters, depending on the nomenclature system employed. In the common name method, in a name such as butyraldehyde, α denotes the carbon next to the CHO. In the IUPAC system the CHO itself is numbered 1; thus, it results that α corresponds to 2, β to 3, etc. Some examples of the naming of aldehydes follow.

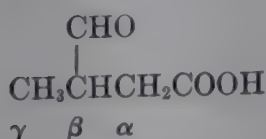




2-methylecyclopentanecarboxaldehyde



1,2,4-butanetricarboxaldehyde

 β -formylbutyric acid

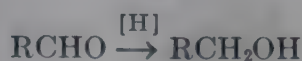
Physical Properties

In the aliphatic series, formaldehyde and acetaldehyde are gases at room temperature, and propionaldehyde (C_3) through hendecanal (C_{11}) are liquids. The boiling points of aldehydes are much higher than those of hydrocarbons with the same carbon skeleton, but below those of the corresponding alcohols. The aliphatic aldehydes from lauraldehyde (C_{12}) up are solids, as are some highly substituted aldehydes, such as sugars (qv), and substituted aromatic aldehydes. The presence of unsaturation or branching in the carbon skeleton tends to lower the melting point. The aldehydes are soluble in alcohols, ethers, and other common organic solvents. Formaldehyde and acetaldehyde are completely miscible with water; propionaldehyde (C_3), butyraldehyde (C_4), and valeraldehyde (C_5) have rapidly diminishing water solubility. The aliphatic aldehydes from caproaldehyde (C_6) up have practically no solubility in water. All of the unsubstituted aliphatic aldehydes have densities less than unity, while most of the aromatic aldehydes are slightly heavier than water. The odors of the aldehydes vary considerably; in the aliphatic series, the lower aldehydes (C_1 to C_7) have pungent, penetrating, unpleasant odors, which become more pleasant as the molecular weight increases. The aldehydes C_8 to C_{14} have pleasant odors and are used in perfumes. Above C_{14} , the aldehydes are almost odorless. The aromatic aldehydes often have pleasing odors. A number of aldehydes are important in the perfume and food-flavoring industries (see Flavors and spices; Perfumes).

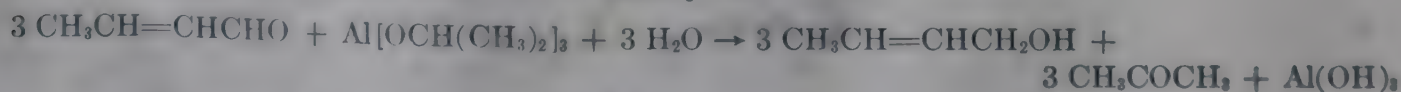
Reactions

The terminal carbonyl group of aldehydes is very reactive, readily undergoing oxidation and reduction and taking part in a variety of addition reactions. Ketones, which contain the carbonyl function at a nonterminal position, undergo similar reactions less readily than aldehydes.

Aldehydes may be reduced to primary alcohols by hydrogenation in the presence of such catalysts as platinum or Raney nickel. They may also be reduced by iron and acetic acid and by lithium aluminum hydride and sodium borohydride.



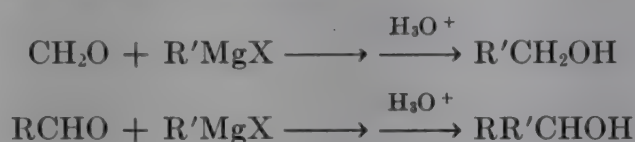
Unsaturated aldehydes may be reduced to unsaturated primary alcohols by means of aluminum isopropoxide (*Meerwein-Ponndorf-Verley reaction*). This reaction is used to prepare crotyl alcohol from crotonaldehyde.



Aldehydes undergo reduction to hydrocarbons, $\text{RCHO} \rightarrow \text{RCH}_3$, by aqueous hydrazine, in the presence of sodium hydroxide and a high-boiling, water-miscible solvent, such as diethylene glycol (*Wolff-Kishner reaction*).

The oxidation of aldehydes, $\text{RCHO} \rightarrow \text{RCOOH}$, is an important chemical reaction and is a commercial method for the production of several organic acids. The carbon skeleton is not altered in the oxidation. The reaction may be carried out in the vapor phase catalytically with atmospheric oxygen, or in the liquid phase by means of an oxidizing agent such as chromic acid. If it is desired to oxidize the carbonyl group of an unsaturated aldehyde, or an aldehyde that contains other readily oxidizable groups, such as a sugar, weak oxidizing agents, such as Tollens or Fehling solutions, are used. These reagents, essentially ammoniacal silver oxide and alkaline cupric oxide, respectively, are also used for the quantitative determination of some aldehydes, including carbohydrates.

Grignard reagents react with formaldehyde to yield primary alcohols and with other aldehydes to form secondary alcohols.



When an aldehyde having no α hydrogen, such as benzaldehyde, is treated with strong alkali, an intermolecular oxidation-reduction reaction yielding equimolar amounts of an alcohol and a carboxylic acid salt takes place (*Cannizzaro reaction*).



Two different aldehydes may undergo a similar transformation (*crossed Cannizzaro reaction*).



A related oxidation-reduction reaction which, however, is not restricted to aldehydes containing no α -hydrogen atoms is the condensation of two molecules of an aldehyde in the presence of an aluminum alkoxide to yield one molecule of an ester (*Tishchenko reaction*). This may be illustrated by the preparation of ethyl acetate from acetaldehyde.



Another reaction generally considered limited to aldehydes containing no α -hydrogen atoms is the *benzoin (acyloin) condensation*, in which two molecules of an aldehyde dimerize in the presence of an alkali cyanide to yield an α -hydroxy ketone, or acyloin. The product from benzaldehyde, for example, is benzoin.



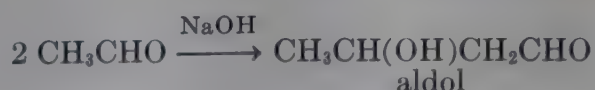
Aliphatic aldehydes do not usually undergo the acyloin condensation when treated with an alkali cyanide. The reaction has, however, been accomplished enzymically. In the presence of yeast enzymes, acetoin has been obtained from acetaldehyde.



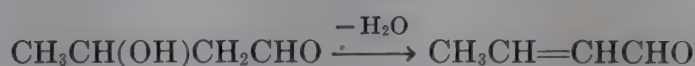
The addition reactions of aldehydes are numerous, but probably all have a common mechanism. The carbonyl group of the aldehyde reacts with a compound HA

(which may be a molecule of the same or another aldehyde, or a ketone, ester, nitro-paraffin, acetylene, hydrogen cyanide, sodium bisulfite, ammonia and its derivatives, hydrazine and its derivatives, alcohols, and thiols) in such a way that H becomes attached to oxygen and the rest of the molecule, A, becomes attached to the carbon atom. Depending on the nature of A, the resulting compound $\text{RCH}(\text{OH})\text{A}$ may be stable, or it may react with another molecule of HA, or it may undergo dehydration to an α,β -unsaturated carbonyl compound.

The base-catalyzed self-condensation of an aldehyde is called an *aldol condensation* and may be shown by the reaction of acetaldehyde with itself to yield the dimer aldol.



The aldol product, on warming or treatment with a trace of mineral acid, is dehydrated to crotonaldehyde.

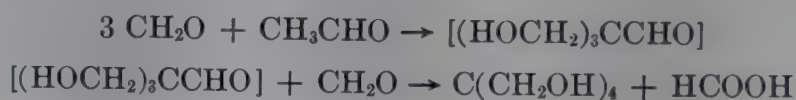


If heating of the aldolization mixture is continued, repeated condensations and dehydrations involving acetaldehyde, aldol, and crotonaldehyde result in the formation of polymeric colored oils and resins.

Mixed aldol condensations between two different aldehydes can also be accomplished. This reaction is generally of preparative value only when one of the reactants contains no α -hydrogen atoms. For instance, acrolein may be prepared in 75% yield from the condensation of acetaldehyde and formaldehyde.



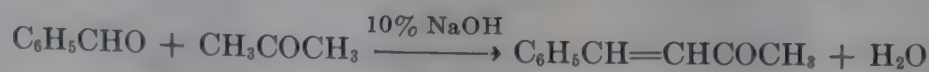
The preparation of pentaerythritol from acetaldehyde and formaldehyde is the result of three aldol condensations followed by a crossed Cannizzaro reaction (see Alcohols, polyhydric).



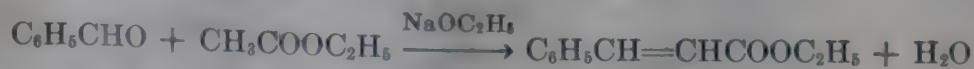
A mixed aldol condensation in which one of the reactants is an aromatic aldehyde is known as the *Claisen-Schmidt reaction*. Aqueous 10% sodium hydroxide is the usual catalyst, and the product is an α,β -unsaturated aldehyde, as illustrated by the preparation of cinnamaldehyde from benzaldehyde and acetaldehyde.



Similarly, an α,β -unsaturated ketone is obtained from the reaction of an aromatic aldehyde with a ketone, as in the following synthesis of benzalacetone.

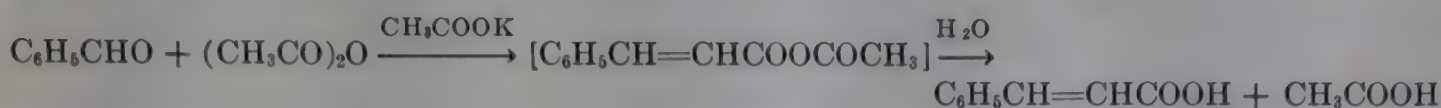


A closely related reaction is the *Claisen condensation* of an aromatic aldehyde with an ester to yield an α,β -unsaturated ester. An example of this reaction is the preparation of ethyl cinnamate from benzaldehyde and ethyl acetate.

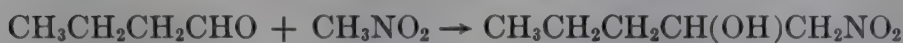
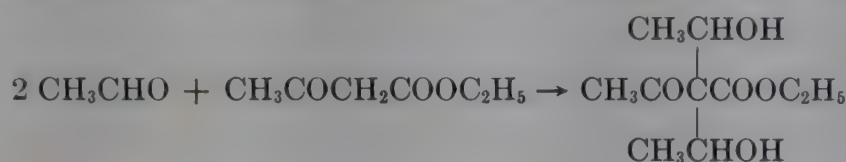
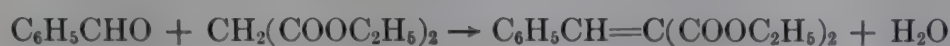


Another condensation restricted to aromatic aldehydes is the reaction of the al-

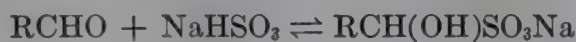
dehyde with an acid anhydride in the presence of the potassium salt of the corresponding acid to yield an α,β -unsaturated acid (*Perkin reaction*). For example, benzaldehyde reacts with acetic anhydride and potassium acetate to form, after hydrolysis, cinnamic acid.



Both aliphatic and aromatic aldehydes readily undergo base-catalyzed addition reactions with compounds having weakly acidic C—H bonds, such as malonic ester, acetoacetic ester, nitroalkanes, and acetylenes. A few examples will serve to illustrate the variety of possible reactions, many of which lead to valuable synthetic intermediates.

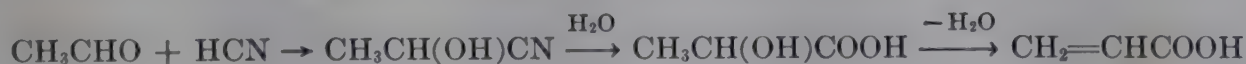


Aldehydes, when treated with a saturated (ca 40%) solution of sodium bisulfite, yield a crystalline addition product.



The reaction is reversible, but the use of excess sodium bisulfite will cause almost complete conversion of the aldehyde to the addition product, a salt which is soluble in water and insoluble in organic solvents. The aldehyde can be regenerated by treating the addition product with dilute acid or sodium carbonate solution. The bisulfite addition products are used to purify aldehydes and separate them from mixtures of organic compounds.

The reaction of aldehydes with hydrogen cyanide yields α -hydroxy nitriles (cyanohydrins), which are useful intermediates in organic syntheses. Cyanohydrins can be hydrolyzed to α -hydroxy acids, which can in turn be dehydrated to α,β -unsaturated acids, as in the following preparation of acrylic acid.



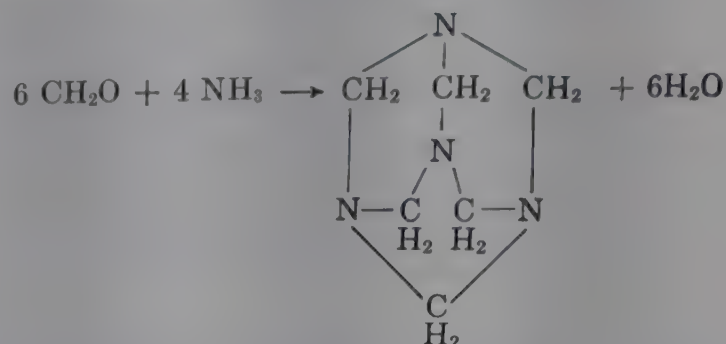
Although cyanohydrins can be prepared directly from aldehydes and hydrogen cyanide, they are usually obtained by treating bisulfite addition products with sodium cyanide. Like bisulfite addition, the addition of hydrogen cyanide is a reversible reaction. Treatment of the cyanohydrin with moist silver oxide will regenerate the aldehyde.

Aldehydes react with ammonia to give addition products, but these are generally too unstable to be isolated. The reaction is utilized, however, in the *Strecker synthesis* of α -amino acids, in which an aldehyde is treated with a mixture of ammonium chloride and sodium cyanide to yield an α -aminonitrile, from which the amino acid is obtained by hydrolysis (see Monosodium glutamate under Amino acids).



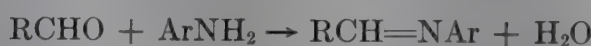


Formaldehyde reacts with ammonia in an exceptional manner to give the tricyclic compound hexamethylenetetramine.



This compound is valuable for it constitutes, in effect, a special form of formaldehyde (qv). It is also used in the preparation of the explosive cyclonite (RDX) and in medicine and organic syntheses.

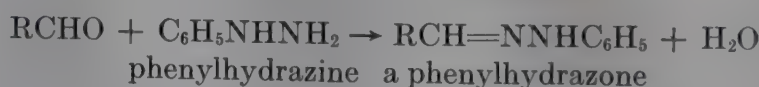
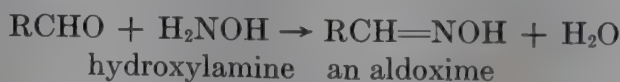
The reaction of an aldehyde with an equimolar amount of an aromatic amine yields a product known as a *Schiff base*, or an *anil*.



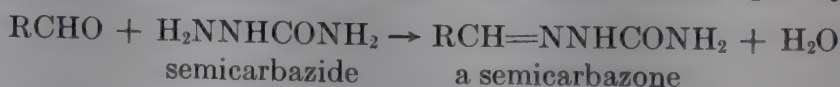
Schiff bases have been utilized as antioxidants and accelerators in the vulcanization of rubber; they are also useful for the synthesis of *N*-substituted anilines.



As indicated by the following equations, aliphatic and aromatic aldehydes react with a variety of other derivatives of ammonia, such as hydroxylamine, phenylhydrazine, 2,4-dinitrophenylhydrazine, and semicarbazide.

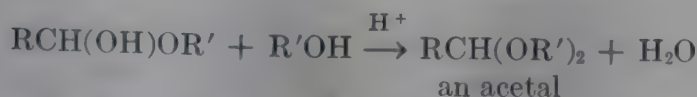
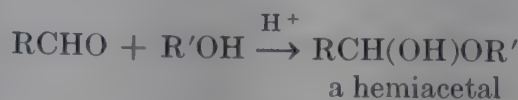


Similarly, 2,4-dinitrophenylhydrazine leads to a 2,4-dinitrophenylhydrazone.

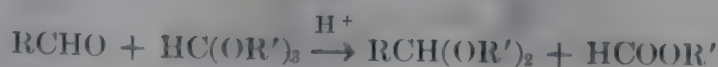


The preparation of aldoximes, phenylhydrazones, 2,4-dinitrophenylhydrazones, and semicarbazones is used mainly for the identification of aldehydes.

Aldehydes react with alcohols under acid catalysis to yield, initially, hemiacetals, which can then be converted by further reaction to acetals (qv).

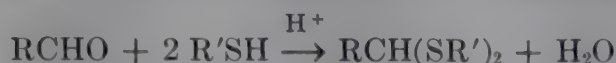


Acetals can also be prepared under anhydrous conditions by reaction of an aldehyde with an alkyl orthoformate.

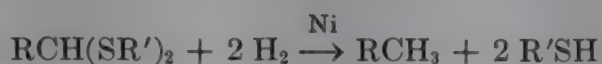


The acetal function is stable to alkali and is used to protect the aldehyde group during reactions, such as oxidation or addition, at another point in the molecule. On completion of these synthetic operations, the aldehyde can be regenerated by treatment of the acetal with water and a trace of mineral acid.

Aldehydes react readily with mercaptans to yield thioacetals.

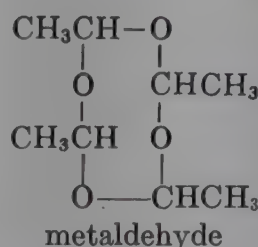
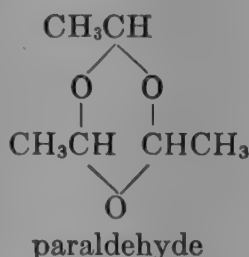
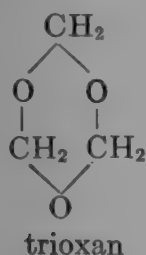


Thioacetals can be reconverted to aldehydes by warming with aqueous mercuric chloride. On treatment with hydrogen and Raney nickel, thioacetals are desulfurized to yield hydrocarbons.



The two lowest aliphatic aldehydes, formaldehyde and acetaldehyde, can be converted into a number of polymeric forms. A linear polymer of formaldehyde, known as paraformaldehyde, $\text{HOCH}_2(\text{OCH}_2)_n\text{OCH}_2\text{OH}$, is obtained by evaporation of an aqueous solution of the aldehyde. Formaldehyde can also form useful polymers of high molecular weight (see Acetal resins). Formaldehyde also forms, under catalysis by dilute sulfuric acid, a cyclic trimer, trioxan.

Acetaldehyde, under similar conditions, forms an analogous trimer, paraldehyde, as well as a cyclic tetramer, metaldehyde.



Heating of these cyclic polymers causes depolymerization and provides a convenient means of obtaining the anhydrous monomeric aldehydes.

Characterization

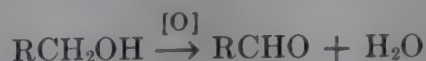
Aldehydes are usually identified by preparation of the oximes, phenylhydrazones, 2,4-dinitrophenylhydrazones, *p*-bromo- or *p*-nitrophenylhydrazones, or semicarbazones. The melting points of these crystalline derivatives are then determined. Aldehydes of high molecular weight may also be conveniently identified by oxidation with potassium permanganate or hydrogen peroxide to the corresponding carboxylic acids. The resulting acids may then be converted to derivatives such as phenacyl esters, amides, or anilides.

Natural Occurrence

Acetaldehyde is found in apples and is a by-product of alcoholic fermentation; none of the other lower aliphatic aldehydes occur in significant amounts in natural products. A few of the higher aliphatic aldehydes and many aromatic ones are found in the essential oils and fruits of plants. Among the naturally occurring aldehydes are: citronellal, in rose oil; citral, in oil of lemongrass; benzaldehyde, in oil of bitter almonds; cinnamaldehyde, in oil of cinnamon; anisaldehyde, in anise; and vanillin, in the vanilla bean. See Oils, essential.

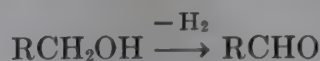
Preparation

Aldehydes may be prepared from a variety of starting materials, such as alcohols, carboxylic acid chlorides and salts, glycols, and olefins. The lower aldehydes may be prepared by oxidation of the corresponding primary alcohols with manganese dioxide or a mixture of potassium dichromate and sulfuric acid.



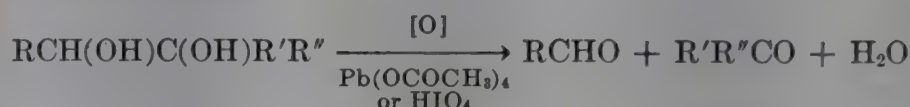
The success of this method depends on the distillation from the mixture of the volatile aldehyde, thus preventing its further oxidation to a carboxylic acid.

Another general method for the preparation of volatile aldehydes, which is of considerable industrial importance, is the catalytic dehydrogenation of primary alcohols.

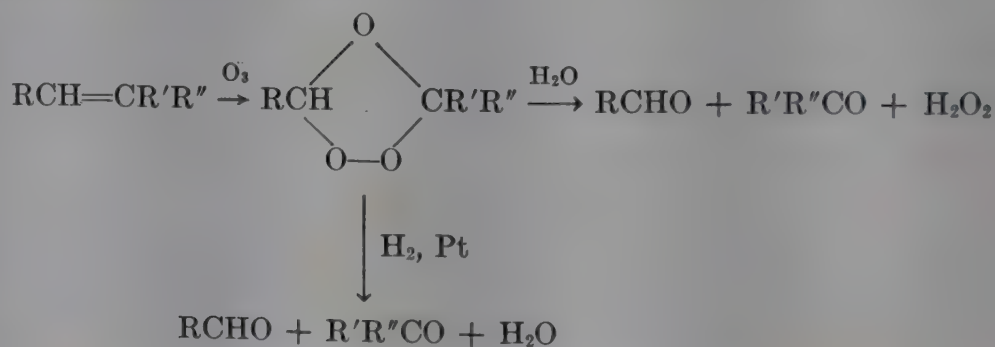


This reaction is ordinarily carried out at a temperature of 200–300°C in the presence of copper or copper chromite.

A vicinal glycol (one containing hydroxyl groups attached to adjacent carbon atoms) may be oxidatively cleaved by lead tetraacetate or periodic acid to yield a mixture of aldehydes and/or ketones.

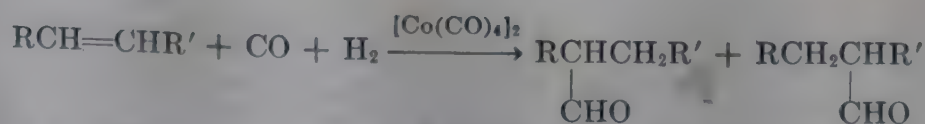


The ozonolysis of olefins is another general method for the preparation of aldehydes. Treatment of an alkene with ozone results in the formation of an addition product known as an ozonide, which may be decomposed by water or catalytic hydrogenation to yield a mixture of carbonyl compounds.



The use of reducing conditions during the decomposition of the ozonide is recommended in order to avoid further oxidation of the aldehyde initially formed.

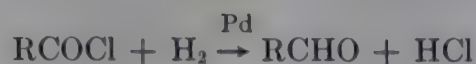
Another procedure for preparing aldehydes from olefins is the *hydroformylation reaction*, which in recent years has achieved considerable industrial importance (see Oxo process). In this reaction, a mixture of carbon monoxide, hydrogen, and an alkene is heated under pressure in the presence of a catalyst such as dicobalt octacarbonyl.



If a terminal olefin, RCH=CH_2 , is hydroformylated, the primary aldehyde, $\text{RCH}_2\text{CH}_2\text{CHO}$, is generally the major product.

Carboxylic acid chlorides also serve as starting materials for the synthesis of aldehydes. The classical method of accomplishing this transformation is the *Rosen-*

mund reduction, in which an acid chloride is treated with hydrogen in the presence of a catalyst (usually palladium) which has been "poisoned" by the addition of a sulfur-containing compound.



A newer method for preparing aldehydes from acid chlorides involves the use of a metal hydride such as lithium tri-*tert*-butoxy-aluminum hydride.

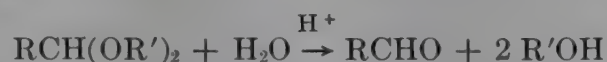


Similar reducing agents can also be used to convert *N,N*-disubstituted amides to aldehydes.

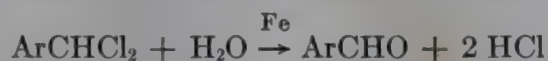


Another general synthesis of aldehydes is the pyrolysis of a mixture of metal (usually calcium) salts of carboxylic acids. This method, which is well known as a means of preparing ketones, has been adapted to the preparation of aldehydes through the use of an excess of a salt of formic acid. Thus, $(\text{RCOO})_2\text{Ca}$ and $(\text{HCOO})_2\text{Ca}$ lead to a mixture of RCOR , RCHO , and HCHO . Distillation of the mixture of products enables the aldehyde to be separated from the less volatile ketone.

Aldehydes may also be prepared by the reaction of a Grignard reagent with an alkyl orthoformate. The initial product is an acetal, which is readily hydrolyzed to the aldehyde with dilute acid.



In addition to the preparative methods described above, there is also a wide variety of reactions which are limited to the synthesis of aromatic aldehydes. One of the most useful of these is the side-chain chlorination of a methyl-substituted benzene to yield a benzal chloride, which is then converted to an aldehyde by hydrolysis in the presence of a catalyst, such as iron powder.



The corresponding carboxylic acid is usually formed as a by-product, the consequence of trichlorination of the methyl group.



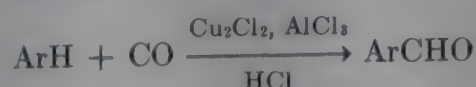
Another important method of aromatic aldehyde synthesis starting from methyl-substituted benzenes is based on a partial oxidation of the side chain. One procedure utilizes a mixture of chromic acid and acetic anhydride; the intermediate benzal acetate is hydrolyzed under acidic conditions to the aldehyde.



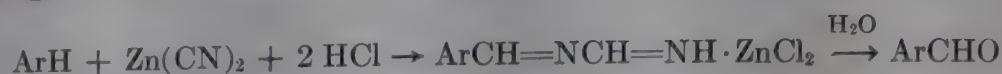
The transformation from hydrocarbon to aldehyde may also be accomplished directly by means of vanadium pentoxide catalyst, or by a mixture of manganese dioxide and sulfuric acid.

The direct formylation of an aromatic hydrocarbon can be accomplished under a variety of conditions. One method is the treatment of the hydrocarbon with a mix-

ture of carbon monoxide and hydrogen chloride in the presence of aluminum chloride and cuprous chloride (*Gattermann-Koch reaction*).



A related procedure utilizes a mixture of zinc cyanide and hydrogen chloride as the formylating agent (*Gattermann synthesis*).

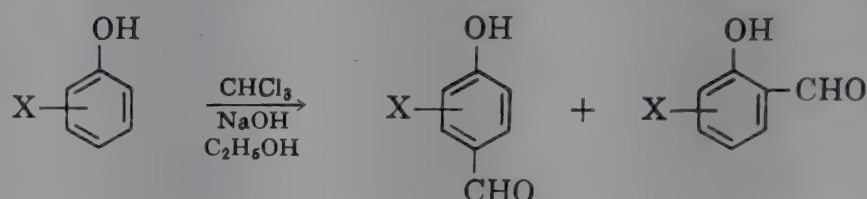


The formyl group has also been introduced into an aromatic nucleus through the use of *N*-methylformanilide in the presence of phosphorus oxychloride.

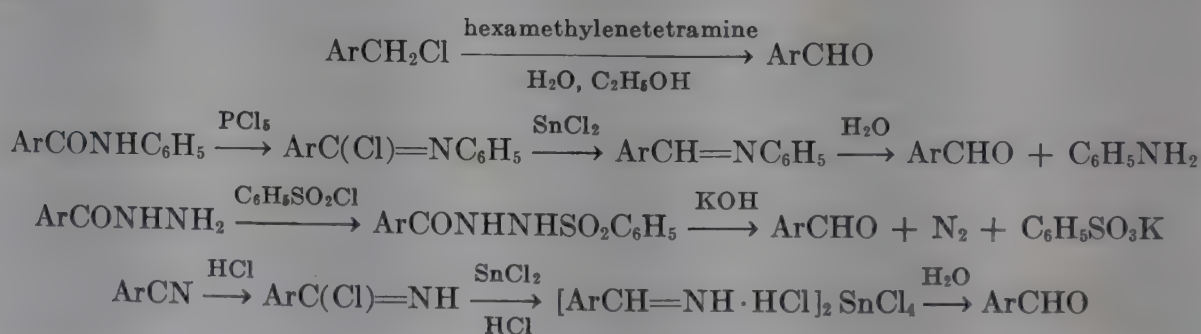


This method is, however, limited to the preparation of aldehydes from phenol ethers, tertiary aromatic amines, and polycyclic hydrocarbons.

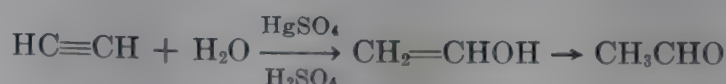
A formylation procedure which is limited to the preparation of phenolic aldehydes is the reaction of a phenol with chloroform and alkali in alcoholic solution (*Reimer-Tiemann reaction*). A mixture of the ortho and para isomers results from this reaction.



As the following equations indicate, aromatic aldehydes may also be synthesized from such varied starting materials as benzyl halides (*Sommelet reaction*), anilides (*Sonn-Müller reaction*), hydrazides (*McFadyen-Stevens reaction*), and nitriles (*Stephen reaction*).



In addition to the methods of aldehyde synthesis described above, many less general procedures, some limited to a specific compound, are known. As an example of such a procedure, the preparation of acetaldehyde by the hydration of acetylene may be mentioned.



"Aldehydes" in *ECT* 1st ed., Vol. 1, pp. 334-342 by E. F. Landau, Celanese Corporation of America, E. I. Becker, Polytechnic Institute of Brooklyn, and O. C. Dermer, Oklahoma Agricultural and Mechanical College.

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ALDOL CONDENSATION. See Alcohols; Aldehydes.

ALDOSES. See Carbohydrates; Sugars.

ALE. See Beer.

ALGAL CULTURES

The artificial culture of algae has been the subject of a number of investigations. The algae can be harvested and used for animal feed and human food. They have long played an important role in the treatment of sewage, and are now being studied in the development of a photosynthetic gas exchanger for human space travel and as a means of concentrating radioactive waste material for disposal.

The algae comprise a heterogeneous group of simple plants of great diversity in size, pigmentation, reproductive mechanism, and composition. They are distinguished from higher plants by a low level of cellular specialization and lack of differentiation into leaf, root, and stem. Some of the larger macroscopic marine algae (seaweeds or kelps) are of economic importance in providing commercial sources of agar and alginic acid. These are excluded from the present discussion since they are harvested from nature and do not submit readily to culture.

The microscopic algae, like other microorganisms, are widely distributed in soils and waters. Although they account for a large fraction of the world's carbon fixation, they are generally dispersed and not notable for accumulation of concentrated masses of organic materials. Their metabolism is based upon *photosynthesis*, a photooxidation of water and reduction of carbon dioxide powered by light absorbed by chlorophyll *a* and various accessory pigments. Like other microorganisms, they are rich in biochemical machinery; they have the highest intrinsic rates of photosynthesis and growth found among the green plants.

The microscopic algae submit to common microbiological procedures. A *pure culture* is obtained as the progeny of a single parent cell. It is maintained in liquid or agarized medium with the usual microbiological precautions for exclusion of contaminants. In some cases it is necessary or desirable to use a single algal species without excluding other microorganisms; this is referred to as a *unialgal culture*. Two culture collections serve as convenient sources for most of the algae which have been isolated (1,2).

Of all the microscopic algae, members of the genus *Chlorella* and the related genus *Scenedesmus* have received particular attention for the purposes of large-scale culture. *Chlorella* will be used as a type case for subsequent discussion although two qualifications of this procedure must be recognized. First, *Chlorella* is only a type case; it is not implied that it will be the alga of choice for any or all applications. Secondly, *Chlorella* is a genus name and includes a number of species and strains, the characteristics of which vary considerably in detail. The particular *Chlorella* most widely studied in the United States is *Chlorella pyrenoidosa* (Emerson strain). It is a hardy and rapidly growing form, an algal weed. Its cells are approximately spherical in shape and 3 to 8 μ in diameter.

History. Pure cultures of algae were obtained by the microbiologist Beijerinck in 1898. Since its introduction by Otto Warburg in 1919, *Chlorella* has become a standard organism for studies on the mechanism of photosynthesis. In the early 1940s Harder in Germany and Spoehr in the United States proposed that practical use might be made of the high synthetic capacities of the algae. They were concerned

primarily with the problem of the world's food supply as extrapolated into the future. Other applications have become apparent; in all of these there are certain common problems and principles of operation.

Algal Growth

Growth of unicellular algae is manifest as an increase in size of each individual cell followed by division into n daughter cells. In some algae $n = 2$ and reproduction is a simple fission of the parent cell. In the *Chlorellas* n lies between 4 and 16, varying statistically within about a twofold limit in any one species and more widely between different species. In other algae occurrence of sexual reproduction may add further complications to the life cycle.

Specific Growth Rate. Under constant environmental (steady-state) conditions algal growth may be described by

$$\frac{dN}{N} = kt \quad (1)$$

or in the integrated form

$$\ln \frac{N}{N_0} = kt \quad (2)$$

where N is some measure of cell quantity, and t is time; k is a first order reaction rate constant or *specific growth rate* with convenient dimensions of days⁻¹. The specific growth rate is a function of temperature, illuminance (or irradiance), nutrient concentrations, and the algal species described. It provides basis for theoretical discussion of controlling conditions and comparison between different algae.

Specific growth rate may be measured in terms of any function of cell quantity, ie, cell number, cell volume, cell weight, or optical density, all of which are related by conversion constants for any one steady-state system. However, cell size and composition of *Chlorella* vary within wide limits as a function of environmental conditions; a steady-state system is maintained only under careful control. A particular problem is illuminance. Mutual shading of cells increases during growth and decreases the effective illuminance per cell even when the incident illuminance is held constant. A steady-state device which dilutes a culture automatically in order to hold constant the cell concentration provides the most effective method of measuring the specific growth rate (3).

Attainable values of specific growth rate vary in different algae over a range of about 1 to 10 days⁻¹ (4,5); the higher values are observed in species capable of growing at higher temperatures (about 40°C). For *Chlorella pyrenoidosa* at its optimum temperature of about 25°C, $k = 2.0$ days⁻¹. Such values are high compared to those of higher plants, but lower than those for many bacteria and yeasts.

Production Rate. As viewed for any culture as a whole, the overall criterion of performance is cell production rate, dN/dt . It is more dependent upon size and geometry of the culture than upon the species of algae used. For evaluation of different cultures or engineering arrangements, it is instructive to refer the rate of cell production to volume or surface area of the culture. Probably the most useful measure of yield is in cell quantity produced per unit time per surface area illuminated (ie, grams/(meter²)(day)).

Cell Concentration. A third criterion of growth is the cell concentration (ie, grams dry weight per liter) at which maximum yields may be obtained. This is important to compactness of the culture and the economics of the harvesting procedure. In nature, cell concentrations attained are never very great and usually preclude the economic harvesting of microscopic algae directly from natural waters. With increase in cell concentration, harvesting procedures become progressively less expensive.

Cell concentration may be measured in several ways. The cell number (cells/milliliter) may be obtained by counting in a hemocytometer under a microscope. Cell volume (milliliters cells/liter) is obtained by centrifuging an aliquot to constant volume in calibrated tubes. Cell weight (grams cells/liter) is obtained by centrifuging an aliquot, washing the cells in water, transferring in minimum volume to a tared crucible, and drying at 110°C to constant weight. (In the present discussion all weights of algae are given as dry weights.) Cell volumes are related rather constantly to cell weights by a factor of 4 or 5 for most algae.

Controlling Factors for Growth

Light. The spectral quality of light utilized by algae for photosynthesis and growth is defined by the absorption of the chlorophylls and accessory pigments. Practically it is limited to the visible region (4000–7000 Å) which comprises about 40% of the total energy of solar radiation. For artificial illumination, choice of commercial sources is based more importantly upon efficiency and intensity than upon spectral quality within the visible region.

Effect of illuminance or irradiance is described by a saturation curve such as Figure 1. Over the early part of the curve, k increases linearly with illuminance; growth rate is *light limited*. At high values of illuminance the curve becomes flat; growth rate is *light saturated*. Two salient points of illuminance are indicated in Figure 1B. I_b designates the small value of illuminance required to maintain the overhead or basal metabolism of the cells. I_s designates the incident illuminance at which the growth rate becomes light saturated. Figure 1A is based upon data obtained by a controlled dilution method using a very thin suspension of *Chlorella pyrenoidosa* growing at 25°C without any nutrient limitation (3). For the filtered tungsten illumination used, I_b is estimated at less than 24 ft-c and I_s at 500 ft-c. There is some uncertainty as to the exact shape of the curve and considerable variation in values of I_b and I_s in different algae.

Carbon Source. Since the algae contain about 50% carbon, this becomes the major problem of nutrient supply. The commonest source is carbon dioxide, 1.8 g of which are required for each gram of algae produced. From data on photosynthesis it is inferred that for a thin algal suspension a plot of specific growth rate vs carbon dioxide concentration will take the form of a saturation curve similar to that of Figure 1, which shows carbon dioxide saturation at $0.15 \pm 0.1\%$. In actual growth measurements on *Chlorella*, k was independent of carbon dioxide concentration from 0.56 to 4.4% (6). Very high concentrations (>6%) are generally considered inhibitory although there are no clearly supporting data. The above data are expressed in terms of composition of the gas phase in equilibrium with the suspension. If rate of carbon dioxide uptake is high, as it may be in a large or dense culture, a considerable diffusion gradient between the gas phase and suspension may be required; hence the common rule-of-thumb use of 5% carbon dioxide in the aerating gas.

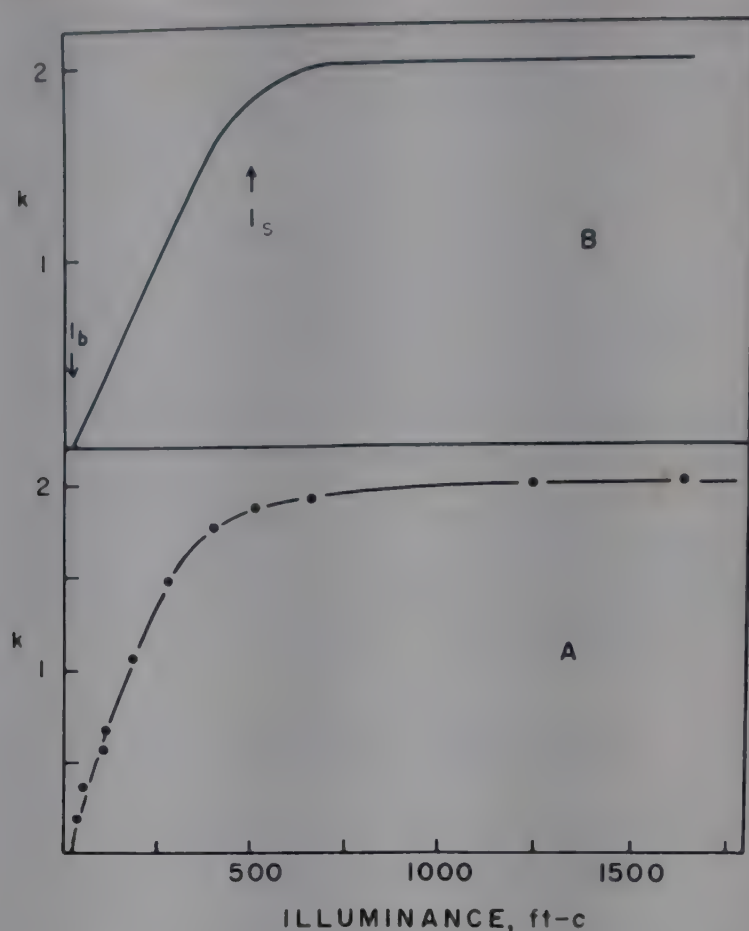


Fig. 1. Specific growth rate k as a function of illuminance. A. Experimental data obtained on a thin suspension of *Chlorella pyrenoidosa* in a steady-state device (3). For the filtered tungsten illumination used, illuminance can be converted to irradiance by the relation 1.0 foot-candle = 41 ergs/(cm²) (sec). B. A simplified curve used for discussion. I_b , illuminance to maintain basal metabolism of cells; I_s , illuminance at which growth rate becomes light saturated.

In addition to carbon dioxide, glucose and acetate will serve as carbon sources for *Chlorella* and many (but not all) other algae; they will support complete and continued cell synthesis (including chlorophyll) in the dark. Cell concentrations up to 36 g/liter have been observed in the author's laboratory for *Chlorella pyrenoidosa* grown in the dark on a medium which originally contained 10% glucose. The specific growth rate was about 0.4 days⁻¹. The simplest laboratory-scale production of *Chlorella* is obtained in flask cultures supplied with glucose and shaken under fluorescent lighting. A difficulty in the use of organic carbon sources is that rigorous pure-culture conditions must be maintained. Otherwise the more rapidly growing molds and bacteria will outgrow the algae.

Nutrient Medium. The liquid medium must provide in stable solution the inorganic ions required for algal cell synthesis. A useful formula is given in Table 1. Except for its nitrogen concentration, it will support growth of *Chlorella* up to cell concentrations of 30 g/liter or greater. For support of lower cell concentrations, the medium may be diluted. The microelements added provide for known or suspected requirements. Unless the water and major salts are specially treated, impurities in them may be as great or greater than some of the microelement concentrations specified. The chelating agent has been found useful in maintaining magnesium and some of the microelements in solution. Essentially it provides a buffered system for the microelements (7,8). If autoclaving is required, the precipitate which forms will not completely redissolve unless the magnesium is reduced to about 0.4 of the concentration shown.

Table 1. Modified Knop's Medium for Chlorella

	Grams/liter	Elemental ppm
major salts		
MgSO ₄ ·7H ₂ O	2.5	
KNO ₃	1.25	
KH ₂ PO ₄	1.25	
chelating agent ^a	0.50	
microelements		
Ca (as CaCl ₂)	0.084	30
B (as H ₃ BO ₃)	0.114	20
Fe (as FeSO ₄ ·7H ₂ O)	0.050	10
Zn (as ZnSO ₄ ·7H ₂ O)	0.088	20
Mn (as MnCl ₂ ·H ₂ O)	0.014	4
Mo (as MoO ₃)	0.007	4
Cu (as CuSO ₄ ·5H ₂ O)	0.016	4
Co (as Co(NO ₃) ₂ ·6H ₂ O)	0.005	1
pH adjusted to range 6.3 to 6.8		

^a Ethylenediaminetetraacetic acid ((ethylenedinitrilo)tetraacetic acid).

Of all medium components, nitrogen is required in highest concentration. The nitrate concentration needed to support a given cell concentration may be calculated by assuming 8% nitrogen in the cells produced. Initial nitrate concentration cannot be increased to more than about 6 g/liter potassium nitrate without initial toxic effects, and development of high cell concentrations may require periodic additions in a batch culture. Nitrate is taken up by the algae effectively as nitric acid which leads to a pH rise with growth. Accordingly, with a pH monitor as gage, nitrogen can be introduced by the periodic addition of nitric acid. Ammonium salts also will serve as a nitrogen source, although they are toxic at lower concentrations and their uptake is accompanied by a pH decrease. A third feasible nitrogen source is urea. It is readily utilized by Chlorella and a number of other algae. It has the merit that it can be used at higher concentrations (to 1%) without toxicity, and its uptake is not accompanied by pH changes in the medium. Among the blue-green algae there are a number of species which fix molecular nitrogen and therefore have no requirement of fixed nitrogen in the medium (9).

The medium formula given in Table 1, while useful for Chlorella, is not to be considered critical in specifications. It is based upon a recipe handed down through years of ancestor worship and tempered with gradual modifications. It contains concentrations that are often much higher than needed. A rational procedure economical of water and salts may be based upon knowledge of the inorganic content of an alga. Cultures have been maintained by periodic centrifuging of aliquot samples, return of supernatant media to the culture, and replacement of the salts estimated to have been removed in the harvested algae (7,10). Table 2 presents the elemental composition

Table 2. Elemental Composition of Scenedesmus

Element	Percent dry weight
nitrogen	6.2-7.4
phosphorus	1.0-1.8
sulfur	0.3-0.4
magnesium	0.4-0.7
calcium	0.03-0.08

of *Scenedesmus* observed in such a recycled culture (10). Variation in composition between algae and under different culture conditions may be much greater than that shown.

Algae differ widely in requirements for nutrient media. Ranges of salt concentrations and pH, which are broad for *Chlorella*, are often narrow. Many algae also require growth factors, notably cobalamin and thiamine, or certain supplementary organic substrates (11).

Temperature. Data are available on specific growth rate as a function of temperature for several algae (12,13). An optimum temperature characterizes each species of alga. From many less quantitative observations, it is clear that many of the algae in culture are relatively low-temperature organisms with optima below 30°C. Directed search for more temperature-tolerant algae has led to isolation of several *Chlorellas*, other green algae, and blue-green algae with optima in the range of 35 to 55°C. The salient point with regard to temperature, however, is that optimum performance of an algal culture requires approximate matching of the temperature and the species of alga. Experience with outdoor cultures in Japan has led to the recommendation that different species be used at different times of the year (14).

Contaminating Organisms. Pure-culture techniques have not been applied to large-scale cultures and have often been omitted from laboratory cultures. Inasmuch as the medium may be essentially inorganic and most algae excrete only small amounts of material, the quantity of bacterial and mold contaminants that develops is always small compared to the quantity of algae and usually has no effect on the algae. Contamination by protozoa and rotifers may be serious since these larger organisms feed upon the algae and may destroy the culture. Chemical control is possible. Low concentrations (about 2 parts per billion) of 2,4-dinitro-6-cyclohexylphenyl acetate and pentachlorophenyl acetate have proved effective (14).

Overall Processes

Synthesis of algal cell material usually is dependent upon the process of photosynthesis. In the past it was conventional to regard photosynthesis as an upgrading of carbon dioxide to carbohydrate, driven by the reducing power which arises from the photochemical oxidation of water. It was supposed that all other algal cell products were produced from carbohydrates by oxidative processes similar to those of heterotrophic organisms. As the biochemistry of photosynthesis has developed, it has become apparent that its essential products are the common biochemical currencies of reduced pyridine nucleotide and high-energy phosphate (as adenosine triphosphate). There seems now little reason to restrict photosynthesis to a synthesis of carbohydrate inasmuch as the essential energetic requirements of other biochemical syntheses are provided. The essential features of this concept are shown in Figure 2. In most algae

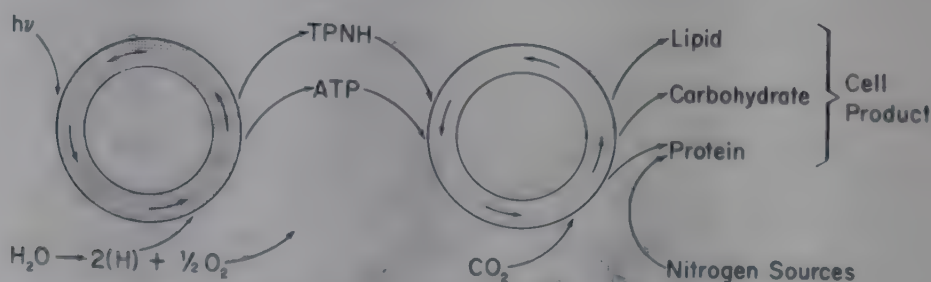


Fig. 2. Simplified flow diagram of algal cell synthesis.

reduced pyridine nucleotide and adenosine triphosphate can also be generated oxidatively in the dark and cell synthesis can proceed from the carbohydrate or acetate that is supplied.

In most algae, excretion of organic matter into the medium is small compared to the quantity of cell material synthesized. In pure cultures of *Chlorella*, excretory materials and wall fragments left by dividing cells account for only about 5% of the total organic carbon formed. Glycolic and oxalic acids and polysaccharides have been identified as excretory products of *Chlamydomonas*; significant amounts of peptide nitrogen are excreted by the blue-green *Anabaena cylindrica*. It may be possible to force excretion of useful products by means of metabolic inhibitors or limited nutrient deficiencies. As a good approximation, however, the normal product of algal synthesis lies in the new cells produced.

Because the excretory products may be ignored and the synthesis proceeds from carbon dioxide, water, and a known nitrogen source, the overall process may be treated as a simple reaction and deduced from the composition of the cells formed. The following data illustrate this. A sample of *Chlorella* was found by analysis to contain 50.44% carbon, 7.0% hydrogen, 9.58% nitrogen, and 8.48% ash. On reducing to ash-free material, obtaining percent oxygen by difference, and dividing by atomic weights, the organic algal product may be written $C_{6.14}H_{10.3}O_{2.24}N$ (formula weight 134, equivalent to a total algal weight of 146). Its formation from water, carbon dioxide, and ammonia may be written,



or, if the nitrogen source is nitrate,



The stoichiometrical relations between carbon dioxide, oxygen, and algal product deduced in this manner have been confirmed by experiment. Such equations are useful in predicting various characteristics of algal culture.

ALGAL COMPOSITION

Treatments of gross composition and the nature and occurrence of special organic components are available (15–18). Gross composition in terms of percentages of protein, carbohydrate, and lipid may be calculated reliably from elementary analysis (18). Summary is difficult since both gross composition and occurrence of special organics vary widely between different groups and species and may vary within rather wide limits even in one species as a function of culture conditions. The more complete data on *Chlorella* and *Scenedesmus* allow approximate summary as in Table 3.

Table 3. Cell Composition of *Chlorella* and *Scenedesmus* in Percent Dry Weight

	Working figure	Lower figure	Upper figure
protein	50	15	70
lipid	15	15	65
unsaponifiable	3	2	4
chlorophylls	4	2	6
carbohydrate	30	15	40
ash	5	2	12

The "working figure" column is presented as a rough guide to composition likely to be found under conditions of maximum yield. The columns for "lower figure" and "higher figure" indicate the direction and magnitude of variations possible by control of culture conditions; however, they are not extreme limits.

Protein. From amino acid analyses (15,16) and from feeding experiments on rats and chicks (15,19), *Chlorella* protein is judged to be of fairly high biological value (60–70 compared to 100 for skim milk protein). Extensive rat feeding experiments on *Scenedesmus* cultivated in sewage in Essen, Germany, place the biological value at a higher level—approximately 100 (20). The protein content of *Chlorella* is normally high (40–60%) unless it is depressed by limitation of nitrogen in the medium.

Lipids. The total lipid content of *Chlorella* is about 15–20% in cells growing without nutrient limitation. Nitrogen deficiency gives rise to cells high in lipid (up to 75%) by virtue of a large increase in the true fat fraction (18). Similar behavior is characteristic of members of several of the algal groups, though not in the red or blue-green algae. Even for the green algae, yields under nitrogen deficiency are so much lower that greater rates of fat production are obtained under normal nitrogen supply. The fatty acids of *Chlorella* are principally C_{16} and C_{18} ; the iodine number varies from about 160 in rapidly growing to 125 in nitrogen deficient cells (21). The chlorophylls *a* and *b*, which normally run 3–5% in *Chlorella*, are depressed by nitrogen deficiency and by high average illuminance per cell. Various sterols in concentrations up to 0.35% have been reported for *Chlorella*, *Scenedesmus*, and other algae. The sterol varies with the species (17).

Carbohydrate. Most of the carbohydrate of algae is in polysaccharides, which vary in type with the species. In *Chlorella* and *Scenedesmus*, most of the carbohydrate is water insoluble. A few of the unicellular algae excrete or produce capsular polysaccharide which may give rise to viscous suspensions.

Vitamins. Most of the important vitamins are present in *Chlorella* and other algae at concentrations sufficient to provide premium value as a food, but probably not at concentrations sufficient to justify extraction (15,18). The blue-green algae contain considerable quantities of the unconjugated pteridine, biopterin (22).

Energy Content. The heat of combustion of *Chlorella* varies within the limits of about 5 to 7 kcal/g depending upon the lipid and ash contents. It may be calculated from elementary analysis or determined by calorimetry (18,23). A figure of 5.5 kcal/g (or 5.8 kcal/g on an ashfree basis) provides a reasonable basis for calculations of efficiency of light utilization.

MAXIMUM EFFICIENCY OF LIGHT UTILIZATION

Two series of measurements (23,24) of maximum efficiency of light utilization by *Chlorella* have yielded values reasonably summarized by the figure $20 \pm 2\%$. As in all statements of process efficiency, the parameters must be defined. *Maximum* efficiency implies that both growth rate and yield are limited only by irradiance. Figure 1 shows that this condition obtains only over the light-limited portion of the curve. The measurement must be made in such a way that no algal cell in the suspension receives an irradiance greater than I_s . Efficiencies obtainable under high irradiance, such as sunlight, are discussed on p. 659.

Maximum efficiency is also a function of wavelength. Light in the 4000 to 6800 Å region (most of the visible) is absorbed by the chlorophylls and is active in photosynthesis. Except for certain pigments other than chlorophyll, all absorbed quanta

within this spectral region are equally effective photochemically. As viewed thermodynamically, the low-energy quanta at 6800 Å (4.2 kcal/mole quantum) are more economical than high-energy quanta of 4000 Å (7.1 kcal/mole quantum). Higher thermodynamic efficiencies will be obtained in red than in blue light. The value of maximum efficiency, $20 \pm 2\%$, was observed in the yellow sodium line (5890 Å, 4.8 kcal/mole quantum). For white light a slightly lower efficiency would be expected. For the spectral distribution of sunlight at the earth's surface, containing about 40% of its total energy in the visible region, a maximum efficiency of 8% ($0.4 \times 20\%$) would be expected.

A third restriction upon the cited value of maximum efficiency lies in the method of calculation. It was based upon the dry weight and elementary analysis of the cells produced. The heat of combustion was calculated from the elementary analysis using a figure of 112 kcal/mole for the oxygen required. Efficiency was calculated as grams algal product times kilocalories heat of combustion per gram divided by kilocalories of absorbed light energy. Since the product is 8–10% nitrogen, efficiencies calculated in this way will vary with the nature of the nitrogen source; they are significantly higher for ammonia or urea than for nitrate (24). The 20% value for maximum efficiency was obtained using nitrate as the nitrogen source.

Weighting of the above considerations leads to reasonable selection of 20% as a working figure for the maximum efficiency of *Chlorella* in visible white light. Accumulated measurements of the quantum efficiency of photosynthesis in various algae indicate that it is doubtful that very large differences in efficiency of total cell production will be found among the different species.

Special Problems of Large-Scale Culture

For large-scale culture it becomes desirable to obtain maximum yields with minimum costs for media makeup and harvesting. The latter consideration depends upon attainment of high cell concentrations. Special attention to media composition is required. When adequate nutrient provision is achieved, attainable cell concentration becomes a function of input rate of light energy and depth or thickness of the suspension.

LIGHT ABSORPTION

Absorption of monochromatic light by an algal suspension may be examined in terms of Beer's law even though a high degree of light scattering imposes severe difficulties in measurement. Beer's law may be expressed

$$\log_{10} \frac{I_0}{I_x} = \alpha cx \quad (5)$$

where c is cell concentration in grams per liter and x is the thickness or depth in centimeters. Values of the specific absorption coefficient, α , for *Chlorella* are listed in Table 4. Absorption $[1 - I_x/I_0]$ is plotted in Figure 3 as calculated from the values of the first column of Table 4. The data do not have any high reliability since pigment concentration (and therefore α_λ) in algae does not have any constant value. However, two important characteristics become evident: (1) Algae have a typically high absorption and (2) cell concentration, c , and depth or thickness of the suspension, x , are reciprocal functions. It has been demonstrated experimentally that the cell concentra-

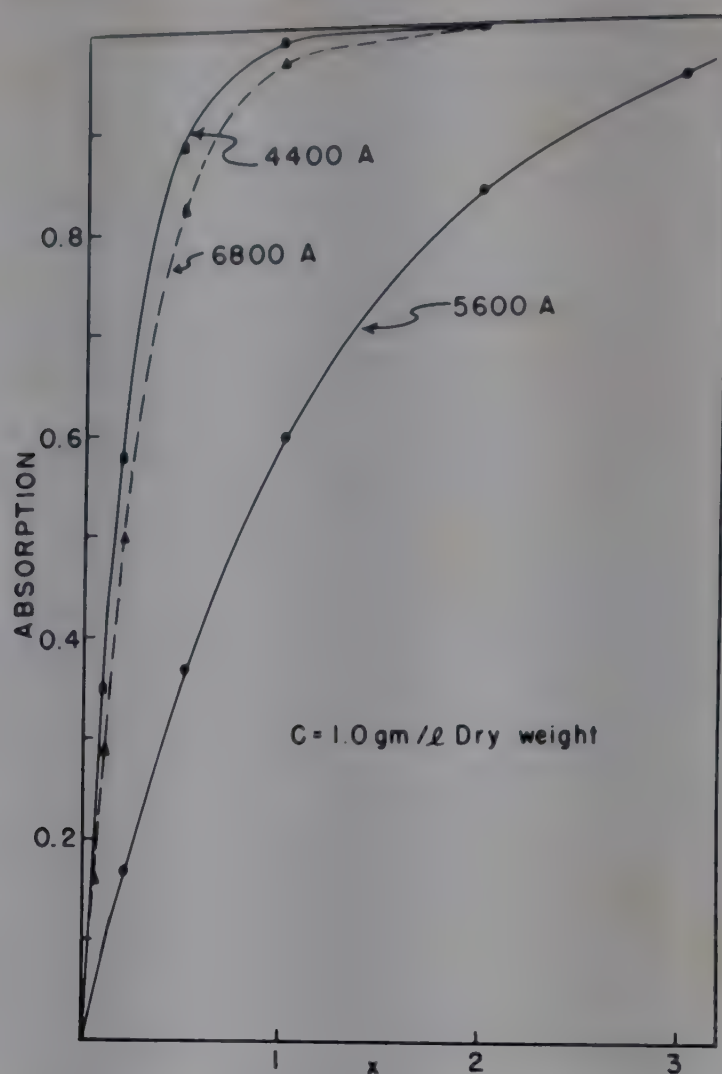


Fig. 3. Absorption of light by a *Chlorella* suspension as calculated from the data of the first column of Table 4 (5).

Table 4. Specific Absorption Coefficients, α , for Suspensions of *Chlorella*

Wavelength, A	<i>Chlorella</i> <i>pyrenoidosa</i> (25)	<i>Chlorella</i> <i>ellipsoidea</i> (26)	<i>Chlorella</i> ; sewage culture (27)
4400	1.9	1.5	
5600	0.4	0.4	
6800	1.5	0.8	
effective average		0.4	0.4-0.9

tion obtainable under sunlight illumination is inversely related to thickness of the algal suspension (8,26). Cell concentrations up to 55 g/liter have been obtained, but only by using very thin (6 mm) layers of suspension. Conversely, deep ponds will support only very low cell concentrations.

The value of cx (grams/1000 cm^2 illuminated surface) that will give maximum yield is not easily calculated. For constant illumination, cx should be great enough to absorb some large fraction of the incident energy. Further increase in cx will decrease yield since some small illuminance per cell (I_b) is required to maintain the overhead of respiration or basal metabolism. In Figure 1, I_b might be estimated at 20-30 ft-c and k at zero illuminance given an equivalent value of about -0.1 day^{-1} . Choice of optimum value of cx requires compromise between completeness of light absorption and minimum effect of the overhead of respiration losses.

SUNLIGHT ILLUMINATION

A particularly difficult problem is imposed by the use of sunlight illumination. In passing through a dense culture, illumination decays with cx , as shown in Figure 4. Two approximations are used for simplicity. First, the decay is drawn according to Beer's law, although for white light absorption the curve must be skewed by variation in α with wavelength. Secondly, light flux is stated in the convenient, though not rigorous, dimensions of foot-candles.

The difficulty demonstrated in Figure 4 lies in the very high illuminance of full

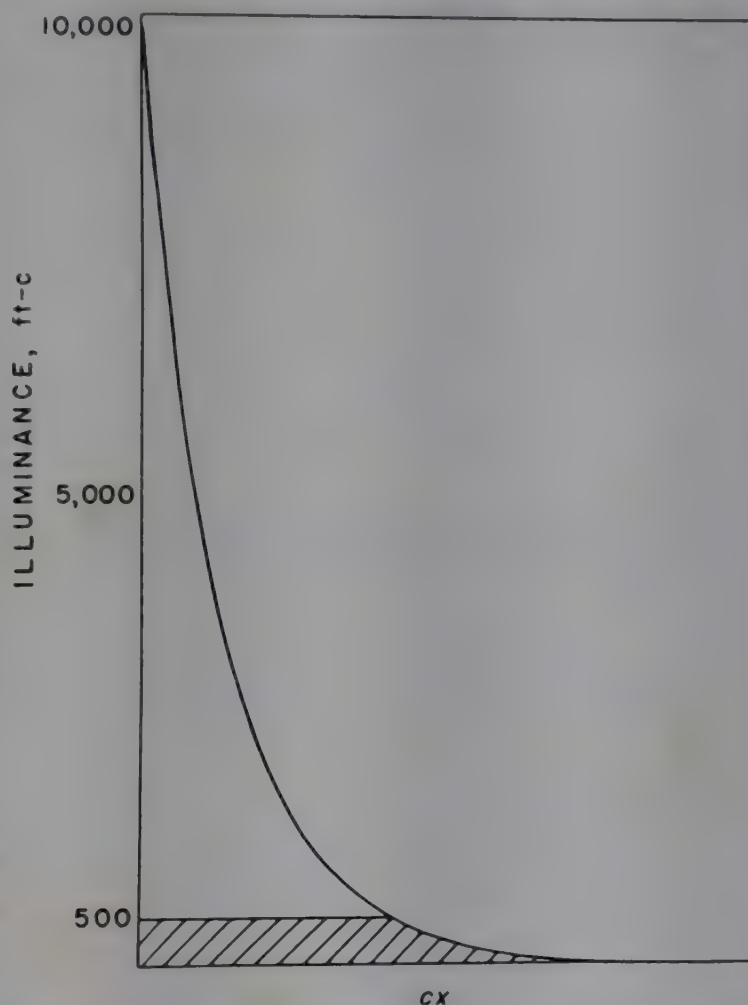


Fig. 4. Illuminance in an algal suspension as a function of cx , quantity of algae per unit area of illuminated surface.

sunlight (10,000 ft-c) compared to the much lower illuminance, I_s (500 ft-c), at which *Chlorella* becomes light-saturated (Fig. 1). A cell at the front surface absorbs light at a rate proportional to 10,000 ft-c, but works photochemically only at a rate proportional to 500 ft-c. From this point the details of the argument depend upon the exact shape assigned to the curve of Figure 1; various treatments have been discussed (5,24,26). The simplest argument illustrating the problem is the following. The total area underneath the curve of Figure 4 is proportional to the total light absorption. The lower shaded area is proportional to the fraction of the light absorption which is used with maximum (20%) efficiency. The fraction of the absorbed light used with maximum efficiency (shaded area/total area), f , may be computed from an equation first derived by Bush.

$$f = \frac{I_s}{I_0} \left(\ln \frac{I_0}{I_s} + 1 \right) \quad (6)$$

From the figures used in the present discussion, $I_s/I_0 = 0.05$ and $f = 0.20$. Efficiency of utilization of full sunlight by *Chlorella* is predicted as $0.20 \times 20\% = 4\%$.

It has been shown that the predictions of the above argument do not fit the results of experimental test very well (28,29). Apparently the main error lies in estimation of I_s , which, in the present discussion, is taken from the irradiance curve for growth (Fig. 1). In most cultures the cells move at random, at rates depending upon turbulence, between the high irradiance of the front surface and the low irradiance in deeper layers. Rates of photosynthesis and growth are locked together as measured over long periods but not over short time periods. As measured over short periods (even as long as several hours), the irradiance curve for photosynthesis does not necessarily match that for specific growth rate. In fact any one alga is characterized by a family of irradiance curves varying in shape with the preceding history of average irradiance per cell. Hence the proper value of I_s , as needed in equation 6, cannot be estimated with precision from the irradiance curve of specific growth rate, and is not a constant character of any one alga.

There also are other complications. It will be recognized that in practice the condition of *full* sunlight is approximated, at best, over only about one-third of the daytime. During most of the morning and afternoon, illuminance on a horizontal surface is far less than 10,000 ft-c and the efficiency predicted by equation 6 will be higher. Practical application of equation 6 is hardly feasible in view of the numerous corrections and integrations required; it is presented only to illustrate the problem.

From various attempts to grow *Chlorella* under sunlight, efficiencies in the range of 2 to 8% have been reported. Such low values are regarded as a consequence of the low light-saturation point (I_s). Attempts to make important gains in yield per unit area must be directed toward this problem. Attempts have been made or suggested in three directions: (a) the use of turbulence of culture to produce advantageous intermittent light effects as viewed by the individual cells (3); (b) the use of light diffusers designed to spread the high surface illuminance over a greater area in the horizontal dimension of a deep culture (29); and (c) the search for algae with equal maximum efficiencies but higher values of I_s (30). None of these attempts has yet proved feasible for economic application.

Practical Applications

Large-scale culture of algae submits to practical application if either the algal product or the attendant gas exchange may be used to economic advantage. Four applications have been developed to various stages of economic practicability.

CULTURE FOR ALGAL PRODUCT

Production of algae for human food, for animal feed, or for special organics is a practical possibility. There are several potential advantages over conventional agriculture: (a) greater possible yield per acre, (b) unlimited growing season, (c) high protein, fat, and vitamin content with minimum wastage in crude fiber, and (d) greater possible control. The criterion of economic feasibility is whether these advantages are great enough to justify the higher installation, control, and processing costs. The problem has been examined by various approaches in England, Germany, Holland, Israel, Japan, Sweden, United States, and Venezuela (31-34).

Laboratory-scale cultures under sunlight illumination have been studied in the usual laboratory flasks and tubes and in larger chambers of varied construction and design: tanks illuminated only through the glass-covered or open upper surface; tanks of glass or lucite illuminated also through the walls; vertical glass or plastic cylinders;

forced circulation through horizontal transparent tubing (32). On a larger scale, approaching pilot-plant operation, three designs have been examined.

Open Bubbling Method. The culture is contained in an open trench or tank and constantly aerated with carbon dioxide-enriched air. This arrangement was studied in Essen, Germany (35). The plant included four culture trenches 70 cm wide \times 20 cm deep \times 9 m long with a fall of 6 mm/m. The trenches were rammed down in loam and lined with plastic. Each trench held 600 liters of suspension at a depth of 9–15 cm. Aeration with 1% carbon dioxide was provided via perforated and coated iron pipes. A similar arrangement was examined in Japan (14). Difficulties inherent in the design appear to be: (a) contamination by rain, dust, and other microorganisms; (b) inefficient use of carbon dioxide; and (c) settling of algal cells.

Closed Circulation Method. The culture is circulated in a transparent plastic tube or in a shallow trench covered with plastic. The method was studied by Arthur D. Little, Inc., at Cambridge, Massachusetts, in an arrangement shown in Figure 5

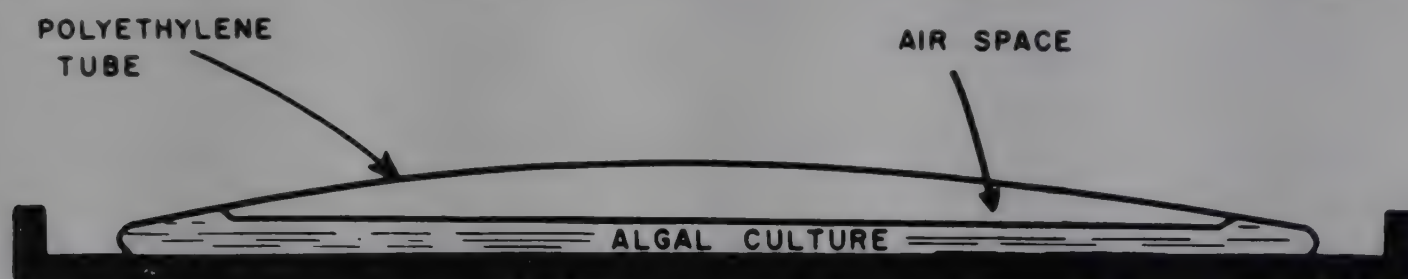


Fig. 5. Algal culture in a plastic tube; closed circulation method (36). Cross section.

(36,37). Flexible polyethylene tubing of 4-mil thickness and 8-ft circumference was laid out to give about 150 running feet and 600 ft² of area. The tube contained 1200 gal of suspension at a depth of about 2.5 in. The suspension was recirculated from input and output ports at a rate of 110 gal/min by a centrifugal pump. Carbon dioxide in air (5%) was constantly bled into the gas phase. Cooling of the suspension by a heat exchanger in the pumping line proved necessary in order to keep the culture temperature below 27°C during summer daytime operation with the low-temperature algae used. A similar arrangement using a plastic-covered trench of about 150 ft² area and containing 250 gal of suspension was examined in Japan (14). Difficulties inherent in the design appear to be: (a) fragility and difficulty of repair of the plastic tube or covering; (b) greater difficulties of heat dissipation; and (c) high power costs required for circulation at a rate great enough to prevent settling.

Open Circulation Method. An open circulation system has been devised and studied in Japan (14,34). A pilot model was constructed as a shallow round pond, 5 m in diameter by 20 cm deep. The 2000 liters of suspension were circulated by a one-half horsepower pump. Suspension withdrawn from a point on the periphery was aerated with a carbon dioxide-air mixture and discharged toward the bottom of the pond via a rotating arm suspended from the center (Fig. 6). Intent of the design is to minimize



Fig. 6. Algal culture by an open circulation method (14). Vertical section. Courtesy Stanford Research Institute.

pumping costs and loss of carbon dioxide. Inherent difficulties in the design lie in (a) contamination by rain, dust, and other microorganisms, and (b) the relatively high construction costs. Subsequently the Japanese Nutrition Association expanded the model to a larger pilot plant using similar ponds 20 m in diameter with a total area of 0.79 acre.

Yield and Cost Estimates. A summary of the operation and performance data for the three designs is given in Table 5. The yield data are affected by many factors other than design. None of the geographical locations used could be considered one of choice for maximum performance. The yield data fall in a range observed in numerous experiments with smaller cultures and might be stated as 8–20 g/(m²) (day) (38). It appears that yields in the range of 12–25 g/(m²) (day) (20–40 tons/(acre)(year)), depending upon geographical location, represent reasonable expectancy with current technology and available algae.

Table 5. Operating and Performance Data for Pilot-Scale Cultures

Type	Location	Volume, liters	Area, m ²	Cell concn, g/liter	Yield, g/(m ²)(day) ^a	Cost estimate, \$/lb ^b
open, bubbling	Essen, Germany (35)	2400	25		5.5	
closed circulation	Cambridge, Mass. (36,37)	5000	55	0.3–0.5	9	0.25
open circulation	Tokyo, Japan (14)	2000	20	0.5–2.0	19 ^c	0.26
open circulation	Tokyo, Japan (34)		3000	3.0	8 ^d	

^a Highest average yield maintained over a one-month period. Multiplying by 1.63 gives tons/(acre)(year); by 8.93, lb/(acre)(day).

^b Projected for 100-acre plant of similar basic design.

^c Yield of 12.5 g/(m²)(day) average for one-year period.

^d Average yield for 300 working days in one-year period.

Cost estimates (Table 5) as of 1955 by Fisher (37) in the United States and Tamiya (14) in Japan are based upon extrapolations of about 10,000-fold to 100-acre plants and cannot have great reliability. However, they are good enough to justify the conclusion that in the United States the cost is too high to merit development as a source of animal feed. In Japan the more critical demand for food and greater versatility of diet makes economic development at least a marginal possibility. Preparations of an algal product suitable for acceptance in the Japanese diet have been produced successfully.

The cost estimates of Fisher and Tamiya are remarkably close (\$0.25 and 0.26 per lb) and fortuitously so since differences in design and location led to quite different cost breakdowns. In both cases a very small fraction of the cost is required for expendable materials and a very large fraction is contributed by a large capital investment (about \$3 million per 100-acre plant). Production costs would be lowered significantly by higher yields or by less expensive construction.

TREATMENT OF SEWAGE

The use of *sewage lagoons* or *sewage oxidation ponds* has proved an adequate and economic means of treatment of domestic sewage in the southern portion of the United States. The profuse algal flora which develops is an essential component. Field and laboratory studies (39–42) have established the following general principles of operation. Two biological agents are involved: algae and aerobic bacteria. As a result of

their photosynthetic activity during the day, the algae bring about a rapid production of oxygen and uptake of carbon dioxide. The high dissolved oxygen concentration, which may reach 25–30 ppm or 300% of air saturation, allows the aerobic bacteria to bring about a rapid oxidation of unstable organic matter to carbon dioxide. At night the algae take up oxygen in their own respiratory processes but their overall activity during the daily cycle affords a great excess of oxygen production and carbon dioxide uptake. The net result is a biologically cyclic process as a result of which sewage organic matter is converted into algal cells.

Depending upon pond characteristics, the algae produced may be discharged in an effluent or may be allowed to settle and apparently digest anaerobically as a bottom sludge. The aerobic surface layer and typically high pH, 8–10, minimize or entirely prevent sulfide production and odor nuisance. When pond effluents are discharged into diluting streams of large volume, the algae usually remain stable and actually may contribute to, rather than detract from, the biological productivity of the stream.

Experience in Texas, based on more than one hundred installations, has led to the following recommendations: (a) a conventional primary treatment device such as an Imhof tank or primary clarifier; (b) pond area to provide a loading of not more than 50 lb biochemical oxygen demand (BOD) per acre-day; and (c) a pond depth of about 3 ft (43). The pond area requirement is equivalent to about 1 acre per 400 persons. The method is considered desirable for the needs of small communities in mild climates. For large cities, land areas and costs become exorbitant.

The simple oxidation pond is a relatively crude operation which requires minimum control or maintenance. Attention has been given to the possibilities of improving performance characteristics. There are two complementary objectives: (a) increased efficiency of operation allowing more compact design and lower land area requirements, and (b) the harvesting of the algae produced as a crop of economic value.

A unit with an area of 50 m² in Essen, Germany (44), using domestic sewage with added carbon dioxide gave yields of 4–11 g/(m²)(day) of algal product containing 28–38% protein. Increased protein content up to 58% was obtained by a small addition of nitrate to the influent sewage. A 70% reduction in organic matter was obtained.

Extensive studies proceeding from laboratory to pilot-plant scale at Richmond, California, have been reported by Gotaas, Oswald, and co-workers (27,40–42). They have worked out design equations checked against operation of a tank having an area of 22 m². Their equations allow prediction of the critical characteristics for optimum performance from values for the biochemical oxygen demand of the influent sewage and the daily insolation (cal/(cm²)(day)). Probable values of the latter have been worked out as a function of month and latitude in the United States. Their equations and experimental results show highest algal yields at rather shallow depths (<30 cm) and at short detention times (1–3 days). They have predicted that a plant in Phoenix, Arizona, should be operated at a depth of about 20 cm and a detention time varying from 2.2 days in summer to 4.1 days in winter. Further extension of their calculations shows that the plant would be loaded at a rate of 180 lb BOD/(acre)(day) and would produce about 110 lb of algae per acre-day.

Some estimate can be made of the possible improvements on the crude oxidation pond. Maximum yields of algae are not likely to be higher than those attainable under mass culture in nutrient media for which a maximum foreseeable value has been estimated at 25 g/(m²)(day) or 223 lb/(acre)(day). (Yields approaching this have been ob-

tained at Richmond, California, over short periods of operation.) Since 1 lb of algae is approximately equivalent to 1.5–1.6 lb of oxygen (see eq 4), it may be estimated that a BOD loading of 350 lb/(acre)(day) is attainable. This is a potential increase of seven-fold over the current recommendation of 50 lb/(acre)(day) for crude oxidation ponds. The harvesting and sale of algal product is attractive as a means of organic reclamation and nitrogen conservation. However, the savings in production costs over growth in synthetic nutrient media occur only in carbon dioxide and inorganic salts which do not constitute a large fraction of current cost estimates. There is also a special difficulty in harvesting since sewage will support only low cell concentrations (<0.5 g/liter), although precipitation with very low alum concentrations has proved effective.

THE PHOTOSYNTHETIC GAS EXCHANGER

The exploration of space demands methods of providing for the requirements of human occupants of a closed chamber. For short periods the requirements can be managed by an *expendable* system in which stored materials are consumed and waste products are absorbed or accumulated. Cost in volume and weight is proportional to time of sustained operation. The practical human requirements can be met by expenditure of materials equivalent to about 10% of body weight per day.

For very long periods of space flight, or for maintenance of planetary bases, some *regenerative* system is needed in which waste products of the human are converted into usable input materials. The gas exchange problem could obviously be met by a photosynthetic plant which accomplishes just the opposite gas exchange as the human—ie, oxygen evolution and carbon dioxide uptake. If pushed to its limit, the idea would suggest an attempt at reconstruction in a small space of the balance of the entire biological world in which foods, exchanged gases, and excreta become balanced by the action of many organisms to form a materially closed system driven by an input of light energy alone. Such a regenerative or closed ecological system would require a fixed cost of volume and weight for components and accessory equipment. The breakpoint in time at which a regenerative system becomes preferable requires evaluation based upon actual engineering development.

Since the components of the human turnover are partially separable, a regenerative system may be approached in various ways. Table 6 shows that the largest human

Table 6. Approximate Human Turnover in Grams per Day

Input		Output	
H ₂ O	2200	H ₂ O	2540
O ₂	860	CO ₂	980
food (dry)	520	solid waste (dry)	60

turnover is in water. Recovery of water, therefore, is the first-order problem for a regenerative system. Regeneration of gases is the second-order problem. Production of food and regeneration of solid waste (45) become third- and fourth-order problems.

A photosynthetic gas exchanger offers the possibility of providing for oxygen and carbon dioxide exchange as a primary objective; as a secondary objective it might provide partially for the food requirement and disposal of excretory materials. There is no doubt whatever that a photosynthetic exchanger can be devised. The question is

whether the space and power requirements can be made small enough to merit practical application. It is attractive in principle though fraught with technical difficulties. Various aspects of the problem of the photosynthetic gas exchanger have been attacked in a number of laboratories. Only a limited amount of experimental work has been published (46–49). Some of the important parameters have been predicted (50,51).

Quantity of Algae Required. The respiratory demand of a man is taken as 25 liters of oxygen per man-hour with a ratio of CO_2/O_2 (RQ) of 0.825. In estimating the photosynthetic gas exchange of algae over long periods, the data reported for short-time measurements of photosynthesis cannot be used. Algae can photosynthesize for periods of several hours, and, by piling up carbohydrate rather than producing complete cellular material, at a rate about twice as high as may be sustained under steady-state conditions. Photosynthetic gas exchange may be calculated reliably from the specific growth rate, k , which can be maintained, and the stoichiometry between cell product and gas exchange as obtained from equations such as 3 and 4. If artificial illumination is used, k must be kept to about one-half of its maximum value. As seen in Figure 1, the incident illuminance should not be greater than I_s ; there will be losses in efficiency for any cells which become light saturated. Conversely, if most of the light is to be utilized, cx (concentration \times thickness) must be great enough to allow a high fractional light absorption. The choice of a half-maximum value for k is not fixed but is reasonable for purposes of the present estimate. For *Chlorella pyrenoidosa* at 25°C, $k_{\max} = 2.0 \text{ days}^{-1}$.

The data of equation 4 may be used for a model calculation. Thus, 134 g organic matter(ashfree) or 146 g dry-weight algae is equivalent to 6.85 moles oxygen; the oxygen equivalent is 1.05 liters/g algae. At a half-maximum growth rate of $k = 1.0 \text{ day}^{-1}$, 1.0 g algae produces 1.05 liters oxygen per day or 0.044 liters oxygen per hour. Dividing into the human demand of 25 liters/hr gives 570 g algae per man. (A corollary is that the exchanger would produce 24 g algae per man-hour.) The use of nitrate instead of ammonia (see eqs 3 and 4) would reduce the figure somewhat. However, choice of nitrogen source must be based on other considerations of nitrogen content and the CO_2/O_2 ratio required.

Volume. The volume of a photosynthetic exchanger is an engineering problem which has not been attacked. As illustrated for *Chlorella pyrenoidosa* at 25°C and 570 g of algae per man, the basic problem to be attacked is the following. At a reasonable concentration of 2.5 g/liter, 230 liters of suspension would be required per man. To obtain desirable illumination, the suspension should be contained in a layer not greater than about 1.0 cm thick as viewed by the illuminating surface. An area of 230,000 cm^2 is required. The problem becomes one of obtaining the largest possible area in the smallest possible volume. Currently available tubular fluorescent lamps would require a tank design in which the lamps are closely spaced. A large fraction of the total volume would be required for the lamps themselves. An alternate design, which sacrifices efficiency for compactness and does not attempt to illuminate a large area, is based upon the General Electric Quartzline tubular tungsten lamp (47,49). However, extensive performance data showed only poor overall efficiency, as evidenced by production of 0.3 to 0.5 g of algae per kilowatt-hour of electrical input. The low yield seems attributable to the low efficiency and very high intensity of the lamp, which results in light saturation of the algae (see Sunlight illumination, p. 659).

Power. Power requirements may be estimated in the following simple fashion:

The rate of total energy output of an average man, equivalent to an uptake of 25 liters of oxygen per hour, is 120 kcal/hr or 0.2 hp. Maximum efficiency for the light-to-chemical energy conversion by algae has been taken as 0.2. Therefore the minimum light power requirement is 1.0 hp of visible light per man. If the available energy source is electrical, then the lamp efficiency must also be included. Maximum efficiency of a usable electric lamp of long lifetime is taken as 0.2 for the fluorescent lamp; this figure does not include ballast losses which may be made very small by high-frequency operation. Therefore the minimum electric power requirement is 5 hp per man, a large power demand of which 96% will appear as heat.

The power requirements for illumination can be eliminated by using solar illumination. Outside the atmosphere the visible irradiance may be estimated at 0.75 cal/(cm²)(min). At an efficiency of 0.2 for the photosynthetic conversion, the human requirement for oxygen of 600 liters/day might be met by an exposed area of 1.5 m². Under continuous irradiance of 0.50 cal/(cm²)(min), an efficiency of 0.05 has been observed experimentally (28). An 0.05 efficiency leads to prediction of an area requirement of 6.0 m²/man. The use of solar illumination is obviously attractive though it poses some severe engineering problems.

Expendable Materials. An exchanger will probably require certain expendable but stable materials. It is assumed that the medium may be recycled and water conserved. At 5% ash and 8% nitrogen content, the rate of algal production would require 1.2 g salts and 2.3 g ammonia, or 4.0 g urea, or 14 g potassium nitrate per man-hour. The nitrogen demand might be reduced by partial use of urea from human urine.

ACCUMULATION OF RADIOACTIVE WASTES

The algae accumulate inorganic ions in a typical and at least partially nonspecific fashion. Superimposed on a normal uptake of potassium, magnesium, phosphate, and sulfate, there occurs an accumulation similar to that of ion exchange resins. Limited laboratory data are available from a study of one alga, *Chlorella pyrenoidosa* (52). For example, Sr⁹⁰⁺⁺ is accumulated by cells of *Chlorella* with a distribution coefficient (moles per kilogram algae per moles per liter of solution) of about 10³. However, the distribution coefficient is suppressed by competing ions (Mg⁺⁺, Na⁺, K⁺) and the presence of chelating agents in the solution. Increased distribution coefficients were obtained after the algae population doubled in a dilute ammonium phosphate solution; the resulting algae appear to be "ionic traps" in which extraneous ions are taken up more rapidly than by normal algae. The principles of the sewage oxidation pond have been used on a subpilot-plant scale to study the problem of harvesting the algae (53). Application of algae to accumulation of radioactive wastes is reasonable in theory but uncertain in practicability.

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ALGIN. See Seaweed colloids.

ALIZARIN. See Anthraquinone derivatives and dyes.

ALKALI AND CHLORINE INDUSTRIES

Introduction.....	668	Bibliography.....	740
Chlorine.....	671	Sodium hydroxide.....	740
Bibliography.....	707	Bibliography.....	756
Sodium carbonate.....	707	General bibliography.....	757

INTRODUCTION

This article describes the manufacture and distribution of commercial chlorine (Cl₂), soda ash (Na₂CO₃), and caustic soda (NaOH). These are the primary products of chemical industries whose basic raw material is common salt. The three products are sold almost wholly to industry for the production of glass, soap and detergents, fibers and plastics, pulp and paper, petrochemicals, fertilizers, solvents, and a host of "chemicals." In fact, the industrial uses are so diverse that there is hardly a consumer

product that is not dependent on chlorine and alkalis at some stage in its manufacture or in the manufacture of its constituents.

The prominence and the vitality of the alkali industries and their place in the civilization of the mid-twentieth century are illustrated by the accompanying tabular comparisons. The U.S.A. tonnage-type product comparison of Table 1 ranks the alkalis well below the giants, but well above the midgets. The per capita data of Table 2 for a few nations, chosen to bracket a wide range of industrialization, show that alkali use parallels the usual assessors of a commercial economy.

For each 1000 tons of NaCl contained in the mineral which the alkali-chlorine industry “mines,” it potentially puts on the market some 900 tons of alkali ($\text{Na}_2\text{CO}_3 + \text{NaOH}$ expressed as Na_2CO_3) and also some 600 tons of chlorine. But man’s

Table 1. Magnitudes and Growth Rates of Large-Scale Chemical Products, U.S.A. Data

Product	1960 Value, millions of dollars	1960 Production, millions of 2,000-lb tons	Tonnage growth rates, % increase per year	
			1925–1940	1945–1960
refined petroleum	15,600	440	5.4	3.8
petrochemicals	11,500	28.1	49.1	15.4
man-made fibers	1,920	0.9	16.1	6.6
aluminum (ingots)	980	2.0	7.7	7.2
chemical wood pulp	650	21.9	6.9	6.1
synthetic ammonia	445	4.8	24.0	10.3
sulfuric acid	332	17.8	3.8	4.6
caustic soda	308	4.9	7.3	7.3
chlorine	293	4.6	12.2	9.4
soda ash	167	5.4	5.8	1.7
phosphates (marketable rock)	117	19.6	5.9	5.9
potash salts	88	2.6	16.6	8.2

Table 2. Alkali-Chlorine in the Economic Life of Several Nations^a

Nation	Population and land			Annual per capita volumes			
	Number, thousands	Total area, thousands of sq miles	Density, no. per sq km of arable land	Gross national product, U.S. \$	Total alkali, $\text{Na}_2\text{CO}_3 + \text{NaOH}$ as lb Na_2CO_3	Chlorine, lb Cl_2	Electric power, kw-hr
Australia	8,987	2,975	69	1,351	31	2.2	2,077
Brazil	68,000	3,286	360	242	11	0.5	295
Canada	16,081	3,852	44	1,903	95	35.0	5,640
India	356,742	1,270	288	76	2.5	0.5	38
Japan	89,276	143	1,495	302	34.1	12.2	870
South Africa	12,671	473	208	398	16.6	3.2	1,391
Common Market ^b	170,862	450	529	1,112	52.8	15.0	1,943
U.S.S.R. including Byelorussia and Ukraine	258,750	8,650	90	682	31.3	6.7	1,045
U.S.A.	179,323	3,676	97	2,538	130	51.0	4,180

^a Estimates are based on numerous sources, both private and public, and represent the period 1956–1961. Not all the estimates are for the same year and not all are equally valid.

^b Belgium, Netherlands, Luxembourg, France, Italy, and West Germany.

demand for the two has never been in that ratio and the relation of the demand for the two has never remained constant, although, during the twentieth century, there has been a unidirectional change, variable in magnitude, for which approximate U.S.A. data are presented in Table 3. The world production, given in Table 4 as a function of the 1929 base, shows the same kind of ascendancy of chlorine.

Fluctuations in per capita alkali uses, as illustrated by Figure 1, show that the alkali industry has a relatively steady growth rate except for setbacks related to the general economy, and that it has been a much more stable operation than steel or cement.

Table 3. Trends of Market Balance of Alkali and Chlorine in the United States

Year	Production in 1,000 tons per year		Growth rates in % per decade	
	Total alkali as Na_2CO_3	Chlorine	Alkali	Chlorine
1900	493	6		
1910	875	20	77.5	233
1920	1,450	70	65.6	250
1930	2,520	200	74.0	186
1940	3,970	670	57.5	235
1950	6,680	2,000	68.3	198
1960	11,630	4,600	74.0	130

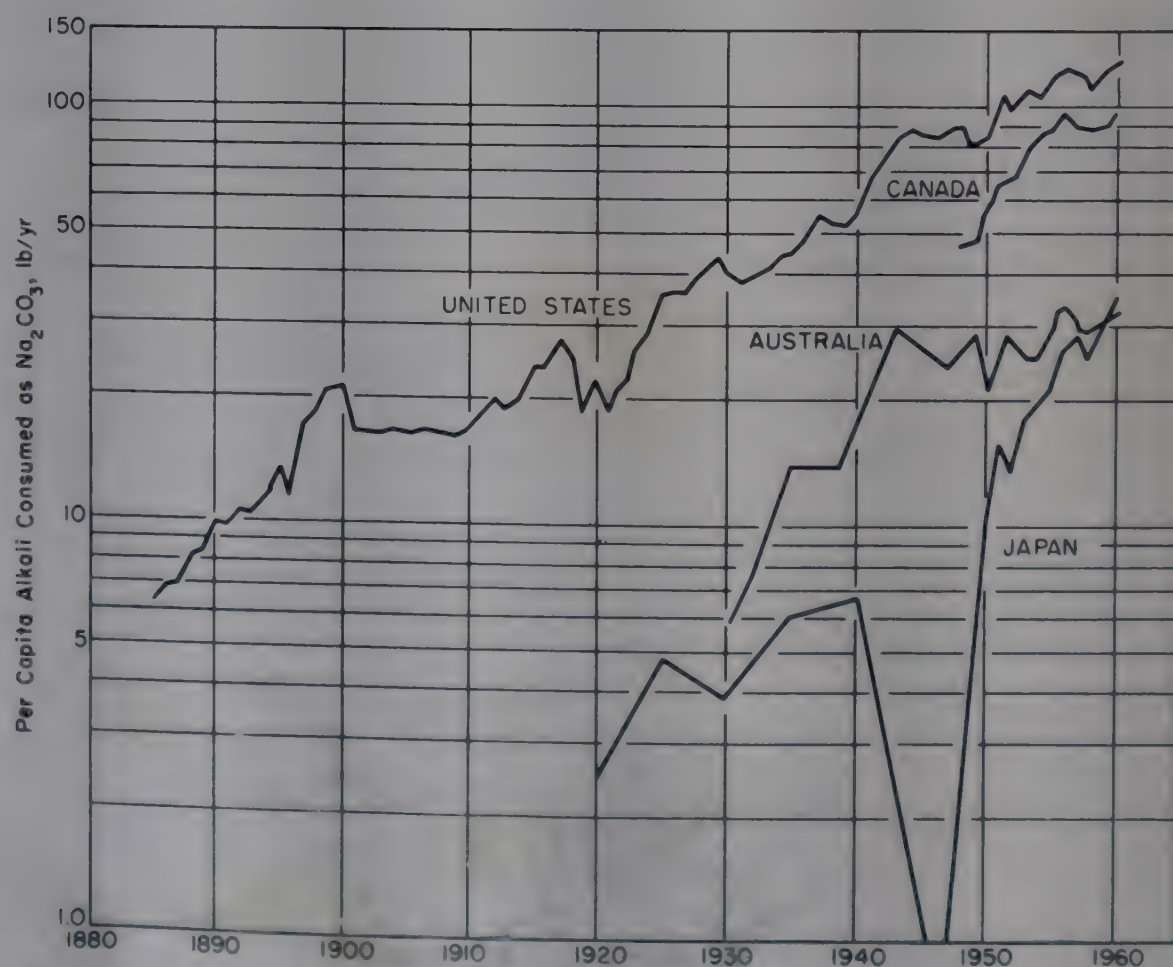


Fig. 1. Per capita alkali consumptions. Total alkali: Na_2CO_3 and electrolytic NaOH (as Na_2CO_3).

Table 4. World Production of Alkalies and Chlorine (1929 = 100)

Year	Soda ash	Caustic soda	Chlorine
1929	100	100	100
1942			476
1949			638
1950	212	400	750
1951	218	413	950
1952	220	432	1,000
1953	220	457	1,100
1954	236	500	1,150
1955	258	518	1,425
1956	266	592	1,525
1957	272	616	1,600
1958	268	598	1,628
1959	298	684	1,728

CHLORINE

Chlorine, element No. 17, is a greenish yellow gas about 2.5 times as heavy as air. Atomic weight 35.453 (¹²C = 12.0000). (On the chemical scale, O = 16.0000, Cl = 35.457.) The two stable isotopes of mass 35 and 37 have natural abundances of 75.53% and 24.47%, respectively. Boiling point is −34.05°C at one atmosphere; melting point, −101°C ± 2°; critical temperature, 144.0°C at 76.1 atmospheres; density of the gas, 3.214 grams per liter at 0°C and one atmosphere. Thermodynamic engineering properties are given in Figure 1, and the density and viscosity of liquid chlorine in Figure 2. (For further properties see Chlorine.)

Substantially all of the industrial uses of chlorine in its early days of commercial importance, beginning with bleaching (the destruction of colored organics), depended on its great chemical activity. Chlorine’s accelerating rate of use in recent decades is not only due to this—elemental fluorine and metallic sodium, both commercially available today, are much more reactive—but to the desirable physical, chemical, and electrical properties obtained when chlorine is substituted into organic molecules.

Chlorine–hydrogen mixtures are explosive within certain limits. All electrolytically produced chlorine contains small amounts of hydrogen along with carbon dioxide, oxygen, and nitrogen. Such impurities are concentrated during the course of liquefaction of the chlorine. Experimental work (1), a correlation of which is shown in Figure 3, indicates that low-order explosions occur when the hydrogen content does not exceed about 18 to 27% of the total, depending on chlorine concentration in the remainder. These tests were conducted at the common liquefaction pressure of 35 psig, using a long tube to allow propagation of a detonation. The low-order explosions showed a pressure rise of less than 100 psi, whereas the detonations reached pressures greater than 2000 psi in only a few microseconds. In order to avoid completely the possibility of explosions, most operators prefer to limit the hydrogen content of any gas stream containing chlorine to not more than 4% hydrogen by volume of total gases. Others may design equipment to withstand the low-order explosions and in that way operate safely with the hydrogen content at a considerably higher level.

Wet chlorine is very corrosive to all of the common metals. Titanium metal is resistant to wet chlorine but is subject to attack from dry chlorine. Wet chlorine is

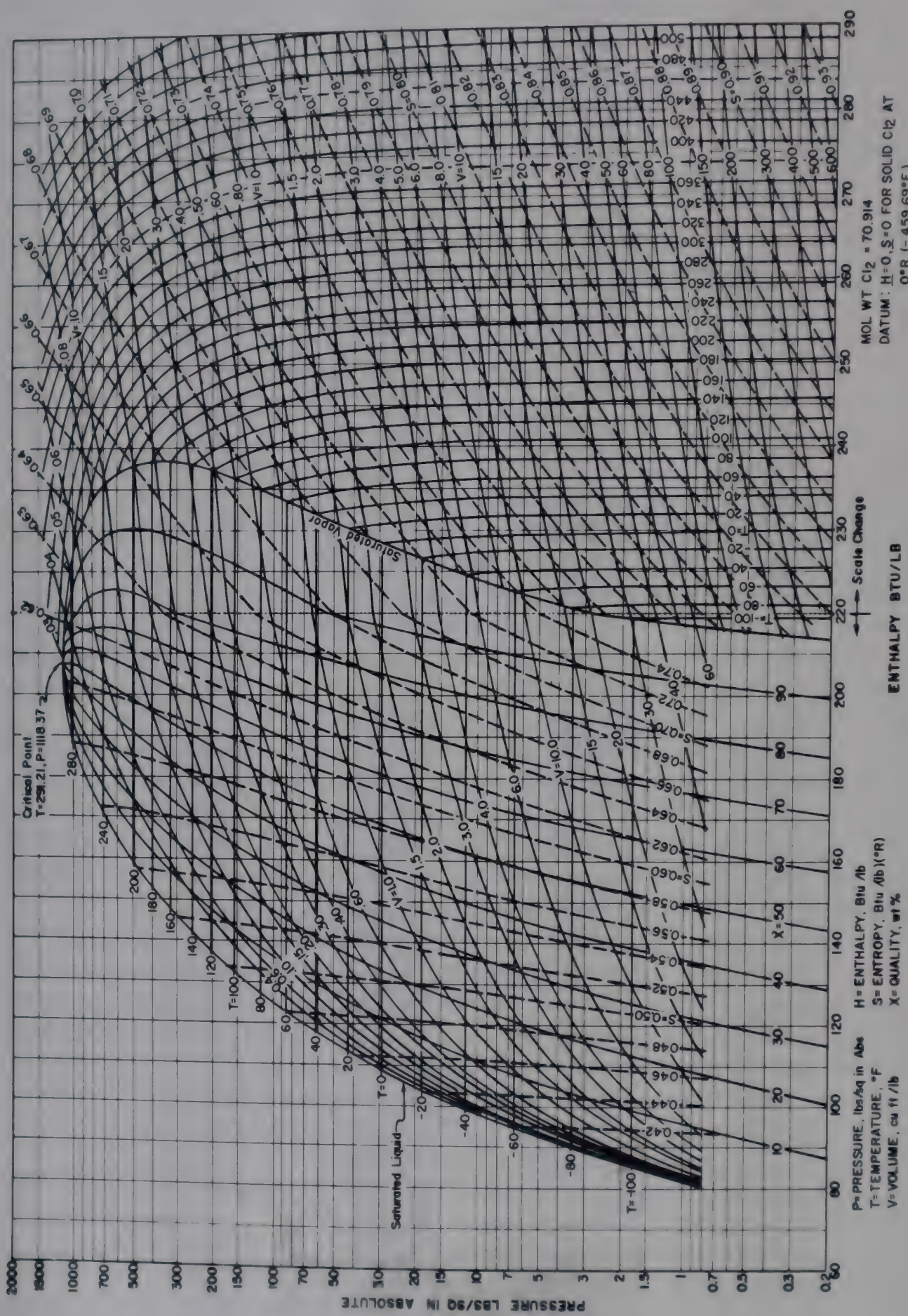


Fig. 1. Chlorine pressure-enthalpy diagram. Plotted from thermodynamic data from Kapoor-Martin (2).

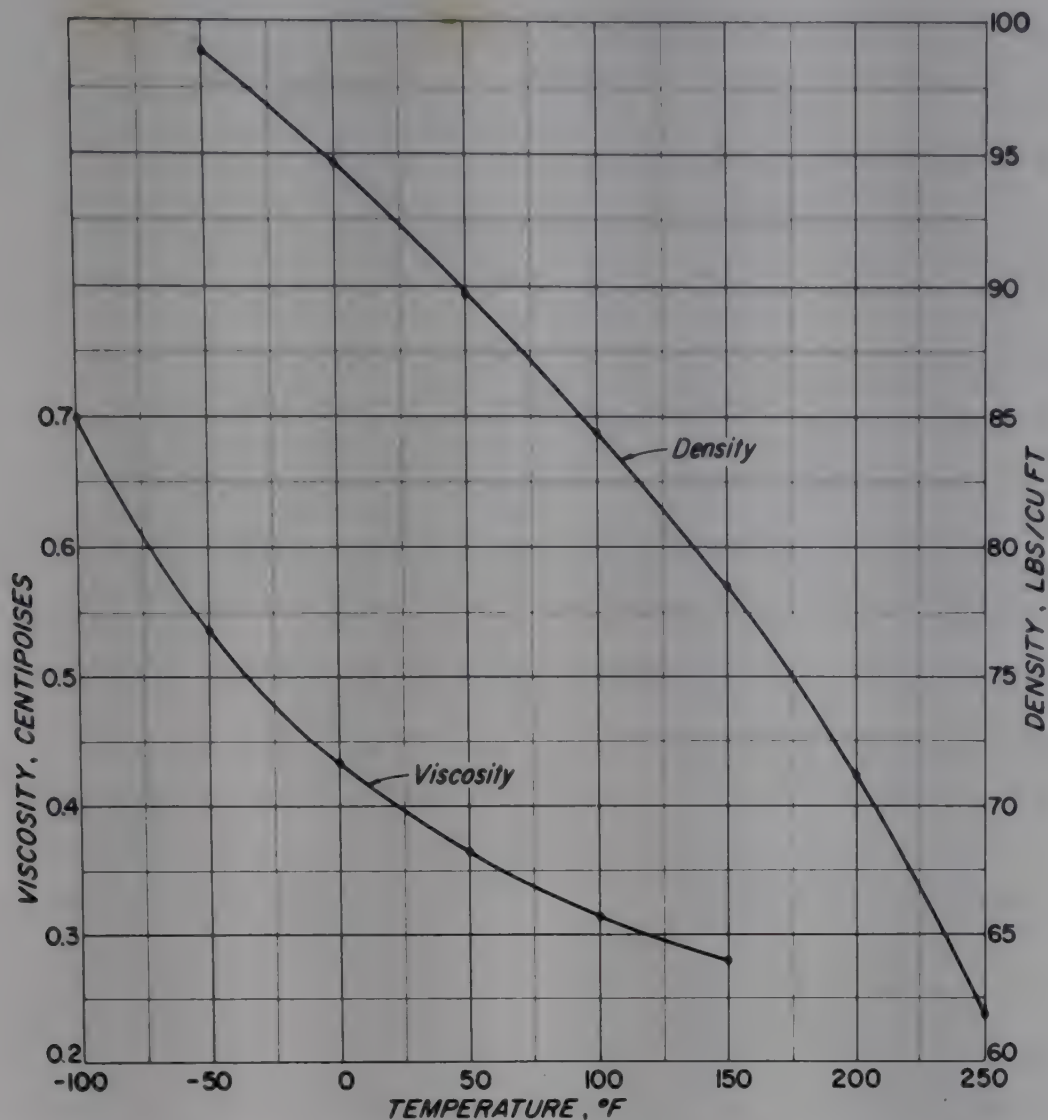


Fig. 2. Density and viscosity for liquid chlorine. Compiled and plotted by Diamond Alkali Co.

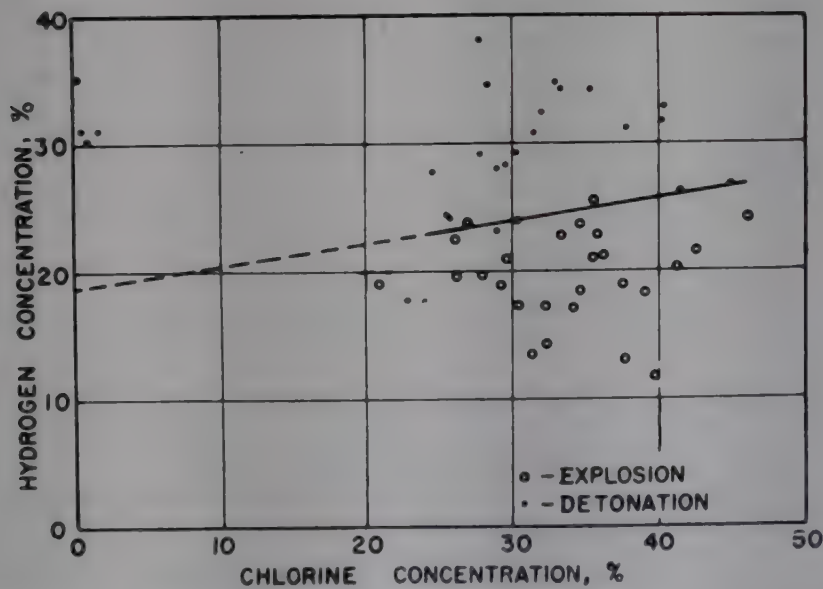


Fig. 3. Explosion-detonation boundary from experimental results. Courtesy *Chemical Engineering Progress* (1).

frequently handled in piping systems constructed of chemical stoneware, glass, and some kinds of halogenated plastics. Dry chlorine, in either the gaseous or liquid state, can be handled satisfactorily in carbon steel at temperatures up to about 250°F. Above 250°F the corrosion rate increases until rapidly accelerated corrosion, and finally ignition, occurs at a temperature ranging from 365°F for steel wool to 485°F

Table 1. Corrosion of Metals in Dry Chlorine^a. Courtesy *Industrial and Engineering Chemistry* (3)

Metal	Approximate temperature at which given corrosion rate is exceeded in short time tests in dry Cl ₂ , °F				
	0.0025 in./mo	0.005 in./mo	0.01 in./mo	0.05 in./mo	0.1 in./mo
nickel	950	1,000	1,100	1,200	1,250
Inconel	950	1,000	1,050	1,200	1,250
Hastelloy B	950	1,000	1,100	1,200	
Hastelloy C	900	1,000	1,050	1,200	
Hastelloy A	900	1,000	1,100	1,200	1,250
magnesium	850	900	950	1,000	1,050
Chromel A	800	900	1,000	1,150	
Monel	750	850	900	1,000	1,000
18-8-Mo stainless steel	600	650	750	850	900
18-8 stainless steel	550	600	650	750	850
platinum	900	950	1,000	1,050	1,050
Hastelloy D	400	450	550		
deoxidized copper	350	450	500	500	550 ^b
carbon steel	250	350	400	450	450 ^c
cast iron	200	250	350	450	450 ^c
aluminum 2S	250	300	300	350	350 ^d
gold	250	300	350	400	400
silver	100	150	250	450	500

^a It is emphasized that these values are based on short-time laboratory tests under controlled conditions. They should be interpreted only as being indicative of the limitations of the materials and should not be used for estimation of the service life of equipment.

^b Ignites at about 600°F.

^c Ignites at 450–500°F.

^d Ignites at 400–450°F.

for steel plate. The corrosion rates of various metals in dry chlorine are given in Table 1.

Most organic matter is attacked by chlorine. The effect on animal tissue is discussed under Health and safety hazards, p. 704, as well as all hazards in the production, storage, distribution, and uses of chlorine.

INDUSTRIAL HISTORY

The first patent connected with any industrial use of chlorine is dated 1799, a quarter of a century after the discovery, and was for its use in bleaching. Even through the next 50 years, chlorine had little industrial importance and affected the lives of very few people. But during the last half of the 19th century, the demand for chlorine for bleaching climbed at a rate that engendered the invention and development of the Weldon and the Deacon chlorine production processes. In both of these, hydrogen chloride (mostly from the sulfuric acid treatment of common salt, the first step in the Leblanc process, p. 710) was the raw material. In the Weldon process, oxidation was conducted with manganese dioxide; the Deacon process used air with a copper chloride catalyst. From both processes the chlorine gas obtained was dilute, but was suitable for making bleaching powder which then served not only as the principal use of chlorine, but also as the only method of transporting the element for use elsewhere.

Toward the end of the 19th century, development of high-capacity, direct-current electric generating equipment took the electrolytic method of chlorine production

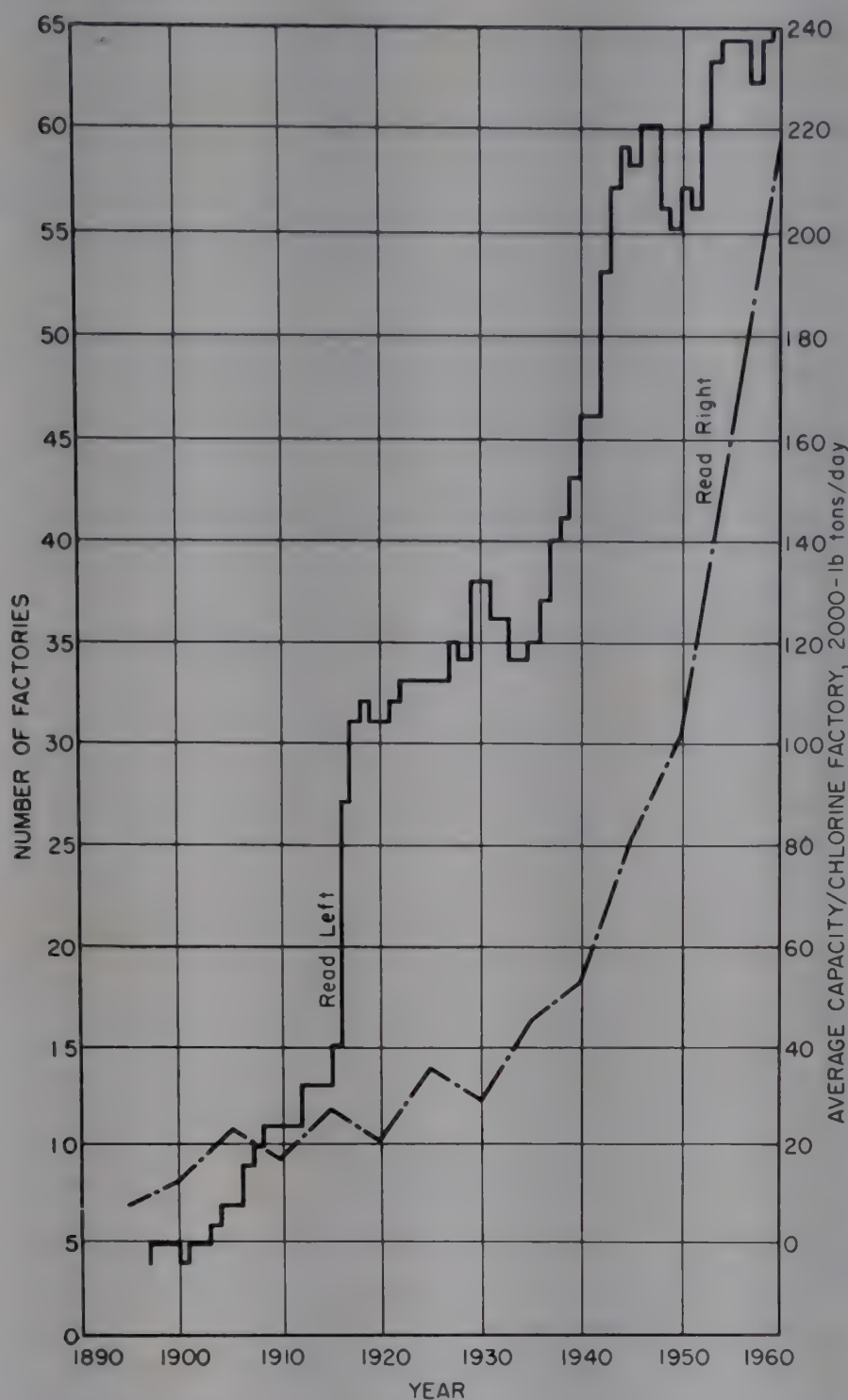


Fig. 4. Number and average capacity of U. S. chlorine factories.

out of the laboratory and into the factory. During the early part of the twentieth century, as alternating-current power distribution took over from the earlier direct-current systems, chlorine plants required current-rectification equipment. The development of this equipment paralleled cell development, though, of course, direct current was also used in many other industries, notably aluminum metal. The earliest rectifiers were motor-generator sets, and synchronous converters, but the mercury arc rectifier became prominent during the late 1920's and by the 1940's it was the leader. The mercury arc rectifier gave the highest energy efficiencies at high voltages. This required the operation of many cells in series, a requirement that put small-capacity factories at a disadvantage. Development of mechanical rectifiers overcame this disadvantage but a notable improvement in rectifiers came with the use of semiconductors such as germanium and silicon for rectification so that, today, high capacities are obtained with relatively few large cells and moderate voltages across cell

banks. Figure 4 shows that at the beginning of the century, the typical U.S. chlorine factory had a capacity of approximately 8 tons per day whereas today it has a capacity in excess of 200 tons per day. From the beginning of the twentieth century, individual cells of a few hundred amperes have been replaced with larger and larger units until 100,000 amperes was common in 1960. Consequently the most pervasive aspect of chlorine's industrial history is that of the technical and dimensional changes in the electrolytic cells used for chlorine production.

At mid-twentieth century, in practically all countries, more than 99% of the chlorine of commerce was produced electrolytically. Table 2 gives the 1959 estimated chlorine production for the principal geographical divisions of the world.

Table 2. Estimated World Chlorine Production for 1959

Geographical area	Thousands of 2,000-lb tons	Percent of total production
All Western Europe	2,110	25.6
Eastern Europe and Western Asia	870	10.6
Asia	605	7.3
North America	4,542	55.2
Latin America	90	1.1
Africa	13	0.1
Australia	11	0.1
<i>total</i>	8,241	100.0

A number of important industrial chemicals are produced as coproducts with chlorine. Sodium or potassium hydroxide and hydrogen are produced from the electrolysis of the corresponding brines. Metallic sodium and metallic magnesium are produced from the electrolysis of the fused chlorides. Sodium nitrate is produced as a coproduct in the treatment of common salt with nitric acid for obtaining elemental chlorine. By far the most important (quantitatively) of these coproducts is sodium hydroxide or caustic soda (see Sodium hydroxide, p. 740). Caustic soda is an older industrial chemical than chlorine. At the beginning of the twentieth century only a small fraction of the NaOH of commerce was produced as a coproduct of chlorine—hardly significant compared to the caustic soda made by the lime process from sodium carbonate. In the U.S.A. in 1940, more than half of the caustic soda of commerce was produced as a coproduct of chlorine. At the peak of the World War II production in the U.S.A., almost two-thirds of the caustic soda consumed was produced electrolytically, and by 1960 this figure had risen to 93%.

In 1960, liquid elemental chlorine was being shipped by all the common methods of bulk commodity transportation. In the U.S., railway tank cars of 16-, 30-, and 55-ton capacity were being employed, and substantial quantities were being shipped bulk via inland waters in 600- to 1100-ton capacity barges. Smaller quantities were delivered in 10- to 15-ton capacity, highway trailer tanks. At a number of locations, chemical complexes operated by more than one owner are tied together with chlorine pipeline transportation (for example, at Ashtabula, Ohio; South Charleston, West Virginia; Calvert City, Kentucky; and along the ship channel near Houston, Texas). Tables 3 and 4 give statistics on the capacity of the U.S. chlorine industry.

In western Europe, the growth of chlorine has likewise been a part of the rapid industrial development following World War II. In most of the large integrated

Table 3. Estimated U.S. Daily Chlorine Capacity in 2,000-lb Tons for Various Coproducts in 1960

Coproduct	Chlorine production capacity	Chlorine marketed as element or new compounds	Percent of total chlorine to market
caustic soda	13,110	11,750 ^a	94.1
sodium metal ^b	755	480	3.8
caustic potash	230	170	1.4
sodium nitrate and nitrogen tetroxide	90	90	0.7
total	14,185	12,490	100.0

^a Includes some 250 tons per day for intraplant use that may not be reported as production.
^b During World War II a portion of magnesium metal production put some chlorine onto the market, but as of 1960 the magnesium industry was a net consumer of chlorine. The amount of chlorine associated with lithium metal is insignificant.

Table 4. Estimated Installed U.S. Chlorine Capacity for Various Processes in 1960

Process	Daily capacity, 2,000-lb tons	Percent of total capacity
diaphragm cell electrolysis	10,842	76.3
mercury cathode electrolysis	2,488	17.6
fused salt electrolysis	755	5.3
nitrosyl chloride	90	0.6
hydrogen chloride electrolysis	30	0.2
total	14,205	100.0

chemical complexes, there is a chlorine plant which serves as a common facility for the various operations.

Chlor-alkali hydrogen is, and will remain during the near future, a minor factor in the total hydrogen picture. The available coproduct hydrogen, equivalent to chlorine production, has generally been in excess of total local demand. Likewise, production of coproduct hydrogen from petroleum refining operations has been in excess of hydrogen requirements for hydrocracking, cyclohexane forming, etc. Thus, in chlor-alkali factories and in petroleum refineries, excess hydrogen is burned for fuel. It was estimated in 1958 that some 75% of the available hydrogen from catalytic reforming operations was burned as fuel, but this figure sank to an estimated 50% during 1962.

The 1960 estimated uses of hydrogen for ammonia and chemical needs, and also the estimated requirements for 1965 are given in Table 5.

The data for the sources of hydrogen used for the biggest single hydrogen customer, synthetic ammonia, indicate that 60% or more comes from steam reforming within the ammonia factory. Not much more than 10 or 11% comes from catalytic cracking, and only about 5% from chlor-alkali operations; some 15% comes from "Texaco oxidation"(4). The remaining 9 or 10% comes from all other hydrogen processes, including pyrolysis of gases, and from low-temperature separations. Thus it is seen that most chlor-alkali factories waste or burn as fuel all of the available hydrogen; a few of the older diaphragm installations do not even have collecting hydrogen manifolds from the cells. Those chlor-alkali factories located near a demand for hydrogen utilize practically all of their production. The 1960 chlor-alkali operations provided less than 10% of the total hydrogen used by industry.

Table 5. United States Chemical (Nonfuel) Uses of Hydrogen (4)

Use	Actual 1960, billion cu ft	% of total	Forecast 1965, billion cu ft	% of total
ammonia	336.0	57.20	470.0	41.41
hydrotreating	155.4	26.40	308.0	27.12
hydrocracking	1.0	0.17	220.0	19.37
methanol	67.5	11.47	80.0	7.04
hydrogenated oils	15.0	2.55	17.0	1.49
naphthalene	0.9	0.15	12.0	1.06
benzene	0.5	0.08	10.0	0.88
cyclohexane	7.6	1.29	10.0	0.88
hydrochloric acid	1.8	0.30	2.4	0.21
space program	1.0	0.17	4.3	0.38
oxo chemicals	0.8	0.14	1.0	0.09
hydrogen peroxide	0.5	0.08	0.8	0.07
<i>total</i>	588.0	100.00	1,135.5	100.00

Methods of Manufacture

Chlorine is produced almost entirely by electrolytic methods from fused chlorides or aqueous solutions of alkali metal chlorides. In the electrolysis of brines, chlorine is produced at the anode, and hydrogen, together with sodium hydroxide or potassium hydroxide, at the cathode. As the anode and cathode products must obviously be kept entirely separate, many ingenious cell designs have been developed and refined. Except for an early period when the bell jar was used, all these designs have been either variations on a type of diaphragm, or else variations on a mercury intermediate electrode.

In the diaphragm process, brine is fed continuously and flows from the anode compartment through an asbestos diaphragm backed by an iron cathode. To minimize back-diffusion and migration, the flow rate is always such that only part of the salt is converted. The hydrogen ions are discharged from the solution at the iron cathode, forming hydrogen gas and leaving hydroxyl ions. This catholyte solution, containing caustic soda and unchanged sodium chloride, is evaporated to obtain the caustic soda; in the course of the evaporation the sodium chloride precipitates, is separated and redissolved, and sent back to the electrolysis.

In the intermediate mercury electrode process, the cation, after discharge, forms an alloy or amalgam with mercury. This amalgam flows or is pumped to a separate chamber in which it is allowed to react electrochemically, most often with water, to form hydrogen and a comparatively strong caustic soda solution containing almost no sodium chloride.

Historically, these two processes were developed during the same decades, although not exactly in parallel. In the United States the mercury process was an early leader, but had shrunk to 5% in 1945; it has since grown toward 20% of the installed capacity. In Western Europe and most other parts of the world, the mercury cell predominates. (See under Comparison of mercury and diaphragm cells, p. 695.)

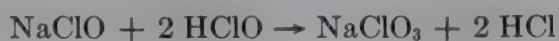
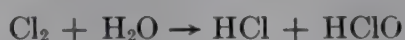
EFFICIENCY OF ELECTROLYSIS

The following discussion is confined to the reactions which take place in commercial chlorine cells, and to the presentation of numerical values of practical engineering constants. Because of its commercial predominance, "brine" refers to sodium chloride brine, unless otherwise stated.

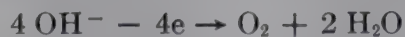
Current Efficiency. Theoretically, 96,500 ampere-seconds (coulombs) produce one gram-equivalent of any material; hence 1000 ampere-hours could ideally produce 2.92 lb of chlorine, 0.0829 lb of hydrogen, and 3.29 lb of sodium hydroxide. In practice these quantities are never fully realized owing to three types of losses inherent in factory operations: (a) current leakages through insulators; (b) secondary reactions; (c) leakages, vaporizations, and spillages of intermediates and products through the entire train from electrode to shipping container. The ratio of the amount of product obtained to the theoretical amount is called current efficiency, and is usually expressed as a percentage. Since this factor is more useful in the comparison of cells than of whole plants, it usually refers to the cell room only, and is most commonly based on the production of caustic soda because of the relative ease of measurement of the quantity of that product. Current efficiency is determined by dividing the pounds of sodium hydroxide produced per thousand ampere-hours by 0.0329, and is typically 95 to 96%.

Current Leakages. Since the operating voltage per cell is low, the insulating problem in a cell should be relatively simple. However, in practice, cells are operated in banks or batteries, with applied voltages up to 600 volts or more, and it is difficult to maintain the full insulating values of "nonconductors" in the presence of conducting salines and corrosive chemicals. The heavy currents call for numerous anodes, the connections of which are subject to corrosion and fouling with conducting chemicals. Furthermore, the best structural materials to resist corrosion by the chemicals being handled in electrolytic cells are not necessarily the best insulators. High operating temperature is desirable to minimize electrolyte resistance, but aggravates corrosion. The cells must be insulated from the ground, and the connections between the feed and discharge streams must also be insulated. All of these problems are, to varying degrees, imperfectly solved, and consequently there is a small loss of current, which is significant principally because of the concomitant corrosion.

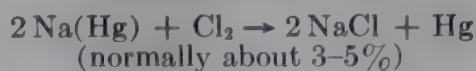
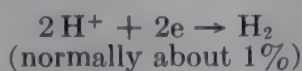
Secondary Reactions (5). It is practically impossible in diaphragm cells to prevent entirely the mixing of anolyte and catholyte, and of course diffusion will always take place, especially across the short distances needed in electrolytic cells to achieve minimum voltage. Furthermore, the electrolyte reaching the cathode contains chlorine in solution. The following reactions in the solution reduce the yield to a small degree:



Other ions in addition to the chloride ion discharge at the anode; the following equations suggest some of the possibilities:



Among these, the principal loss is due to the migration of hydroxyl ions through the diaphragm (5). Other secondary reactions occur in mercury cells.



The nature of these reactions is dependent on the impurities present in the anolyte, the circulating mercury cathode, and the graphite anodes. Usually the current efficiency of a mercury cell is no higher than, and in many cases not as high, as that of the diaphragm-type cell. Impurities present in the anolyte also produce side reactions which affect current efficiency.

Leakages and Losses of Product. Because of the inherent mechanical limitations of structural materials suitable to the corrosiveness of wet, warm chlorine gas, the closures and the packings in cell assemblies and connections cannot, with tolerable capital expenditure, be made as tight as is possible in simpler operations. Also some chlorine is lost in the condensed water which is removed during cooling and drying of the gas. Furthermore, since chlorine is shipped as an extremely pure material and the cell gas is much less pure, a loss is entailed in the various purging operations. These losses are minimal in modern factories, and are almost completely eliminated by the addition of appropriate facilities for recovering the chlorine from purge streams (6). Caustic losses also occur because of entrainment in the hydrogen gas, occasional leaks, and spillages in the caustic collection system. In diaphragm cell plants, caustic losses occur because of entrainment, occasional leakage, and various purges required in the caustic concentration and salt removal operations.

Energy Efficiency. The decomposition potential of sodium chloride in diaphragm cells is 2.3 volts and in mercury cells 3.17 volts. The energy efficiency of cells is obtained by multiplying the current efficiency, expressed as a percentage, by 2.3 for diaphragm cells and 3.17 for mercury cells, and dividing by the mean cell operating voltage of the installation. Voltage and power losses in the cells and cell rooms are discussed under each general cell type.

Kilowatt-Hours Per Unit of Production. From a practical operating standpoint in chlorine plants, the kilowatt-hour consumption per unit of production is by far the most revealing factor. It is comparable to the pounds of fuel consumed per kilowatt-hour of net station sendout in power plants. Like all other practical overall figures, there is a considerable variation from plant to plant in the basis of computing the kilowatt-hours per unit of production. In U.S. practice, it is common to give direct-current kilowatt-hours per ton of chlorine leaving the cell room. Usually this figure represents the energy required for electrolysis only—that is, it does not include consumptions of auxiliaries or the losses of transformers and rectifiers. In Western Europe it is common to refer to kilowatt-hours per metric ton of caustic soda. Rectifier losses may or may not be included in this figure. As summarized in Table 8, p. 696, in the modern 1960 cells, the direct-current kilowatt-hour per 2000-lb ton of chlorine varied from 2680 for lightly loaded diaphragm cells to 3500 for heavily loaded mercury cathode cells.

One of the principal objectives of cell design is to minimize current losses and over-voltages. Other important objectives are (a) to produce a high yield per unit of overall plant investment; (b) to minimize maintenance and repairs; and (c) to minimize attendance labor. Much progress is being made in accomplishing these objectives by reducing the resistance of the current-carrying parts of the cell, by designing for a closer and more uniform spacing between anode and cathode, and by designing large-capacity cells so that fewer units are required for a given production level. Improvements in cell design continue to be of enough significance to permit plants to improve profits even when replacing operable cells with new modern units.

Up to 1945 there had been some 350 U.S. patents on caustic-chlorine cells.

Hardly 10% of these (when considering distinct types) had been reduced to commercial practice and only about one half of that 10% were able to survive the combination of engineering imperfections, insufficient capital, and unfavorable commercial conditions. Between 1945 and 1960 some 70 new patents on the chlorine-caustic electrolytic art were issued in the U.S.A. Many of these 70 were concerned with refinements of design details and with detailed process improvements rather than with basic new concepts of electrolysis or radically different cell designs.

Of these 70 more recently issued patents, almost half have been brought into commercial practice which is quite different from the one-tenth or so of all earlier United States cell patents which achieved commercial application. Up to 1945 approximately two-thirds of the patents were concerned with diaphragm cells and the remainder were concerned with mercury cathode cells. From 1945 to 1960 this patent activity was divided about equally between the two cell types.

Diaphragm Cells

Diaphragm cells of 1960 design can conveniently be divided into two general types: those containing unsubmerged diaphragms; and those containing submerged diaphragms. There are, or have been, types that differ from these two general types and, of course, there are many variations of these two types. In general, both consist of an outer steel shell, either cylindrical or rectangular, which supports a cathode of perforated iron plate or woven iron screen inside of this shell. This constitutes the cathode assembly. The actual cathode surfaces are generally lined with a layer of asbestos either in the form of paper or of vacuum-deposited fibers. At minimum practical distance, graphite anodes are supported so that their faces are parallel to the diaphragm. An inert insulating cover, containing a brine inlet and a chlorine outlet, closes the cell. There is considerable interest in the use of platinized titanium anodes in the place of graphite. Cell performance would be improved because a fixed minimum gap would be maintained between cathode and anode instead of the continuously increasing gap that occurs as the graphite anode wears away. A few commercial installations of platinized titanium anodes have been made (7).

Brine is maintained in the anode compartment at a level above the active electrode surfaces. It percolates through the diaphragm into the cathode compartment where a somewhat lower and adjustable level of dilute caustic is maintained in the submerged type of cells and where it drips off the bottom of the cathode in the unsubmerged type of cells. In either case the hydrogen formed at the cathode is led off from a connection near the top of the outer steel shell from the space between the shell and the cathode. The submerged diaphragm cell has an advantage in that the flow of brine over the entire face of the diaphragm is substantially equal whereas it is highly variable in the unsubmerged type of cell. The submerged type also has the advantage of providing some control over the caustic concentration in the catholyte. Most cell designers now prefer the submerged type.

The function of the diaphragm is to maintain the NaOH strength, and to minimize the diffusional migration of hydroxyl ions into the anolyte and yet approach minimum electrical resistance. An extremely large number of tiny pores is desirable in order to increase output per unit of physical size. However, since the flow through each diaphragm pore must be sufficient to prevent, or at least largely to prevent, the migration of hydroxyl ions, it has been found that, for a given current, the efficiency of a

cell goes through a maximum as the rate of brine flow is varied. This is illustrated for a specific cell in Figure 5. The point at which current efficiency achieves a maximum depends upon the characteristics of cells and diaphragms.

All practical diaphragms gradually clog with the residual impurities that have not been removed from the brine and also with particles of graphite from the anodes. The usual practice is to purify the brine as thoroughly as is economical (see under Brine purification, p. 698) and to renew the diaphragm at regular intervals.

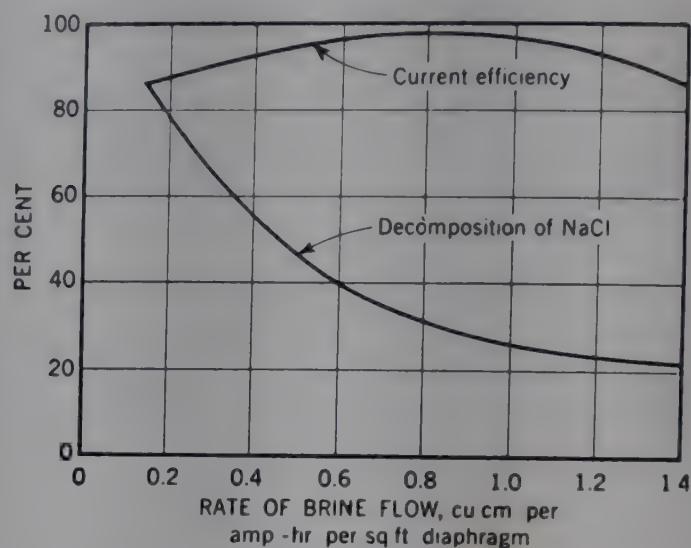


Fig. 5. Effect of rate of brine flow on current efficiency and percent decomposition of NaCl.

Artificial graphite anodes (see Carbon) are in almost universal use in chlorine cells. The graphite anode is used up in alkali-chlorine cells at rates ranging from 5 to 12 pounds graphite per ton of chlorine produced. This includes the loss inherent in removal of anode stubs at replacement time, which amounts to 25 to 40% of the original weight. The rest of the anode loss is due, in about equal amount, to chemical oxidation and mechanical disintegration or erosion. There have been numerous studies of the mechanism of anode disintegration and various expedients have been found to minimize it at the expense of slightly higher voltage. Carbon dioxide formed at the anode contaminates the chlorine gas. Since graphite is slightly porous, oxidation occurs within the pores, thus causing disintegration. Anode life of most modern diaphragm cells is improved by impregnating the graphite used for anodes. The graphite manufacturer uses proprietary sealants and processes. A higher degree of purification of the anolyte and more precise mechanical alignment minimize graphite consumption. Nascent chlorine attacks graphite slowly; the "gum" content of commercial chlorine contains C_2Cl_6 .

Causes of Increased Voltages. In all practical cells the voltage is found to be much higher than the theoretical decomposition voltage of 2.3; numerous analyses of this energy loss have been made. The whole voltage across the diaphragm cell consists of the following main components: (1) the anode potential, consisting of the equilibrium potential plus the chlorine overvoltage; (2) the cathode potential, consisting of the equilibrium potential plus the hydrogen overvoltage; (3) the resistance drop through the electrolyte; (4) the resistance drop through the diaphragm; (5) the resistance drops of the anode and cathode assemblies; (6) the resistance across the electrical contacts; and (7) the diffusional potential. Each of these will be discussed briefly.

The Anode Potential. This depends on the equilibrium potential and also on the chlorine overvoltage. The equilibrium potential is dependent on the temperature as well as the chloride ion concentration. The chlorine overvoltage depends on the nature of the anode surface as well as the temperature and current density. Table 6 gives the chlorine discharge potential with different electrodes at several temperatures.

Cathode Potential. The equilibrium potential for hydrogen discharge is 0.82 volt, which is affected in practice by the concentration of the electrolyte and the temperature. The hydrogen overvoltage also changes with the nature of the cathode surface, the current density, and the temperatures.

Table 6. Chlorine Discharge Potential Using Various Electrodes
(NaCl: 260 grams/liter; 34.8 oz/gal)

		Chlorine discharge potential, volts									
Current density		Magnetite			Artificial graphite				Platinized metal		
amp/sq m	amp/sq ft	25°C	50°C	75°C	16°C	25°C	50°C	75°C	16.5°C	50°C	75°C
100	9.3	1.85	1.75	1.74	1.47	1.43	1.38	1.33	1.36	1.34	1.34
200	18.6	1.90	1.80	1.79	1.55	1.49	1.44	1.35	1.37	1.35	1.35
300	27.9	1.95	1.84	1.82	1.59	1.52	1.47	1.38	1.37	1.35	1.35
400	37.2	1.98	1.87	1.87	1.61	1.55	1.48	1.40	1.38	1.36	1.35
500	46.5	2.01	1.90	1.90	1.63	1.58	1.50	1.42	1.38	1.36	1.35
600	55.7	2.04	1.92	1.91	1.65	1.61	1.51	1.44	1.39	1.36	1.36
700	65.0	2.10	1.94	1.92	1.67	1.64	1.52	1.45	1.39	1.37	
800	74.3	2.12	1.96	1.93	1.70	1.66	1.53	1.46	1.40	1.38	
900	83.6		1.99	1.94	1.72	1.68	1.54	1.47	1.40	1.38	
1,000	92.9		2.01	1.95		1.70	1.55	1.48	1.41	1.39	

NOTE: More recent data are given in refs. 21 and 22 which cover a wider range of current densities useful in modern cells.

Resistance Drop Through the Electrolyte. From the anode to the diaphragm, the electrolyte is a solution of sodium chloride saturated with chlorine and has variable amounts of chlorine bubbles dispersed through it. It is, however, only negligibly different in resistance from industrially pure, saturated sodium chloride solution. A cell design that would reduce the resistance drop through the electrolyte to a minimum is still being sought.

Resistance Drop Through the Diaphragm. This resistance increases with the age of the diaphragm. With a diaphragm 0.05 in. thick at a current density of 0.5 amp per sq in. and a temperature of 75°C, the resistance accounts for 0.12 to 0.15 volt. In the more massive modern cells this resistance may run as high as 0.25 volt.

Resistance Drop of the Anode and Cathode Assemblies. In most practical cells these resistances are low, usually resulting in a total of 0.10 to 0.12 volt. The largest part of this drop is through the graphite anode and varies with the degree of depletion of the anode. The resistivity of graphite is about 0.0004 ohm-in. (0.001 ohm-cm).

Resistance Across Contacts. Graphite-to-graphite, as well as metal-to-graphite contacts have a resistance that depends on the pressures with which the two are held in contact. At 1000 psi, the resistance between graphite and copper is 0.0000555 ohm per sq in. Graphite-to-graphite joints have contact resistances as follows:

<i>Pressure, psi</i>	<i>Contact resistance, ohm/in.²</i>
25	0.000473
75	0.000261
150	0.000175
250	0.000101
400	0.000064
750	0.000036
1,000	0.000031

Diffusion Potential. When two solutions of different compositions meet at a boundary, a potential is set up. In the diaphragm type of cell there should be a drop in potential at the diaphragm where the solution of sodium chloride meets the solution of sodium chloride and sodium hydroxide. This potential has always been less than the errors in its measurement.

The following brief descriptions and historical sketches of the modern types of diaphragm cells in use in 1960 are intended to illustrate the design principles involved rather than to give engineering comparisons of their merits or demerits.

Dow Cell. The cell developed by the Dow Chemical Company and used in Dow plants has a number of unusual features. In 1960 Dow was the largest single chlorine producer and used substantially all of its chlorine in captive operations. The cell consists of a bipolar design which usually results in the erection of blocks of fifty cells; each block operates as a single unit. This is in contrast to the single-cell units employed in other types of diaphragm cells. In the Dow cell, the electric current passes through a multiple-unit series without electrical cables or bus bars between cells. The butting frames are pressed together (similarly to a filter press) to form a tight block. Each cell unit is connected electrically to the next cell unit within the frames constituting the multiple cell block. Chlorine and hydrogen gases are each collected in inverted trough, concrete headers on top of the cells, and caustic is collected at the side through a trap.

Impregnated graphite anodes interleave with vertical, flat-wire-screen cathodes having deposited diaphragms. In operation the anode compartments are kept full of electrolyte and the cathode compartments are kept partly full by means of an adjustable overflow. The operating characteristics of the cell have not been published; the Dow cell is omitted from the comparative tabulation of cells (Table 8).

Diamond Alkali Cells. Diamond Alkali Company, from 1945 to 1947, developed a rectangular, vertical cathode diaphragm chlorine cell rated at 20,000 amperes and, more recently, a cell of similar design rated at 30,000 amperes. During 1960 the 20,000-ampere cell was used only by Diamond in a plant with an installed capacity of about 600 tons per day. The 30,000-ampere cell was in use not only by Diamond but also by Pennsalt Chemicals Corporation and Wyandotte Chemicals Corporation. The total chlorine capacity of these cells was about 650 tons per day.

The base of the cell consists of a shallow cast-iron pan housing flat copper grids. The copper grids and impregnated graphite anodes are imbedded in lead and the lead is sealed with protective coatings.

The cathode assembly consists of a rectangular steel shell housing an inner assembly of lateral rows of vertically flattened wire-screen tubes, upon which a diaphragm has been deposited by suction from a water suspension of asbestos fibers. These rows of screens fit between the anodes when the cathode is lowered onto the

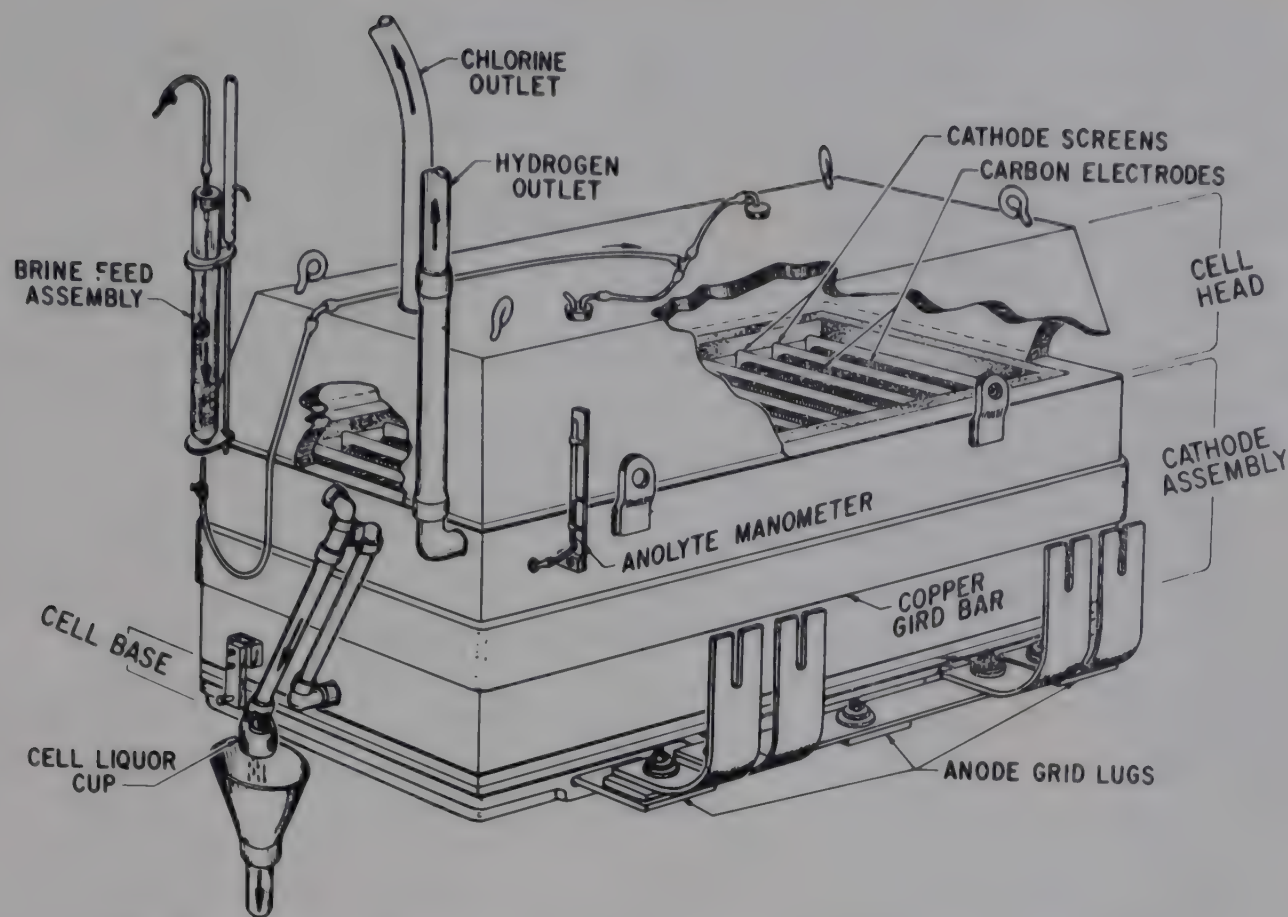


Fig. 6. Diamond D-3 chlorine cell. Courtesy Diamond Alkali Company.

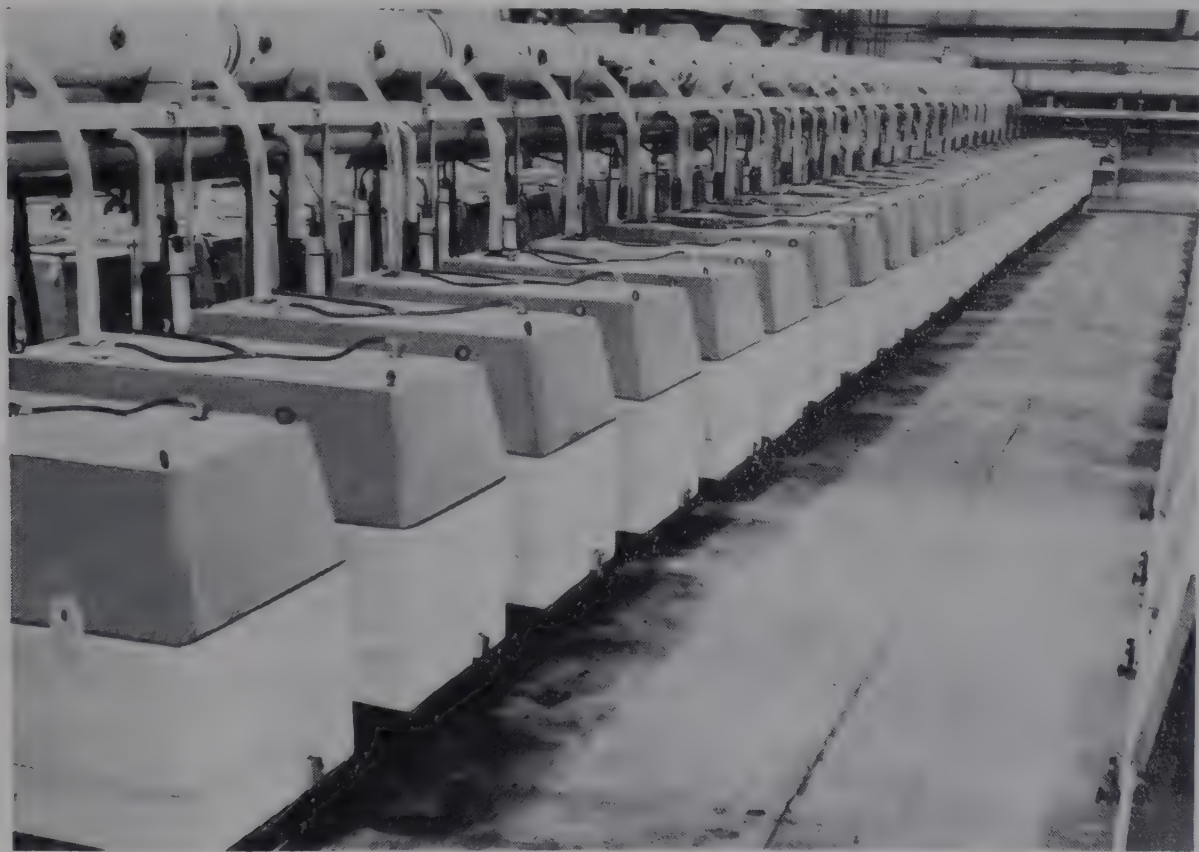


Fig. 7. A Diamond cell installation showing the cell renewal aisle. Courtesy Diamond Alkali Company.

base, thus forming the anolyte and catholyte sections of the cell. The cell is completed by placing a concrete head upon the cathode assembly. The head contains the chlorine outlet and brine feed inlet. Electrical connections are made to a copper bar around the outside of the cathode and to lugs which extend from the anode grids.

This cell is designed so that when anode or diaphragm renewal is required, the cell is cut out of the electrical circuit by a jumper switch, and then the complete cell is removed from the cell room. It is taken to a cell renewal area where it is rehabilitated by production-line methods, thus minimizing costs. (See Figs. 6 and 7.)

Hooker Cells. A 6000-ampere deposited diaphragm cell was developed by the Hooker Chemical Corporation from 1924 to 1934. This basic "Type S" cell has been scaled up and improved, resulting in a series of cell designs. These cells have been used by Hooker and a number of U.S. and foreign firms. The sizes have increased, until the latest (S-3D in 1962) is being offered for operation at 40,000 amperes or higher.

The cell is nearly cubical in shape and consists of three sections—bottom, middle, and top—placed one on top of another. The anode assembly includes a concrete bottom in which is placed a casting of lead which contains the flat copper anode connector bars and vertically projecting graphite anode blades. The lead casting system is sealed into the concrete bottom by a mastic system of asphaltic material.

The cathode section consists of a steel frame with flanged top and bottom; a copper conductor bar is welded to the frame. A steel screen structure, including vertical fingers, is welded to the inside of the steel frame forming an integral cathode unit. The cathode, with deposited diaphragm, is placed over the impregnated anodes and a concrete cell top is placed on the cathode (see Figs. 8 and 9).

Pittsburgh Plate Glass, Chemical Division (formerly Columbia-Southern Chemical Corporation), licensee of the Hooker-type cell, has designed a modification of it. It is designed with fingers extending all the way across as in the Diamond cell. Various size units have been designed up to 30,000 amperes in capacity. In other respects the cells operate essentially as the Hooker cell.

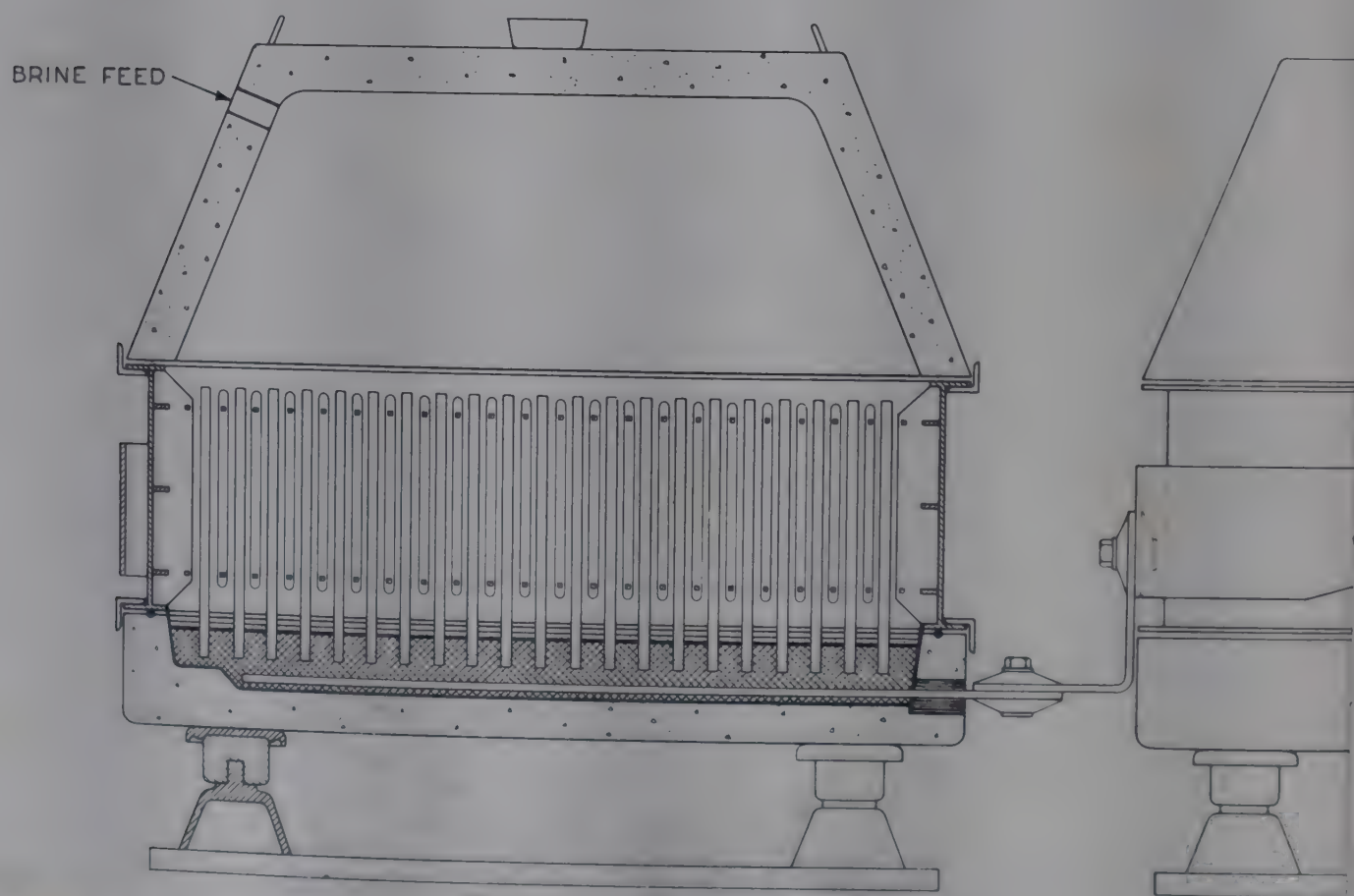


Fig. 8. Hooker Type S-3D, 40,000-ampere cell. Front sectional elevation. Courtesy Hooker Chemical Corporation.

Cylindrical Cells. A group of cylindrical cell types similar to each other, known as Gibbs, Wheeler, Vorce, and Tucker-Windecker, represents smaller outputs and older designs. They still had significant, though rapidly waning, importance in 1960. The Vorce cell is the most widely publicized and also the most widely used cell of this type. It consists of a steel vertical cylinder that forms an outer shell for the cell. Inside the shell and concentric with it, is a perforated steel cathode cylinder clamped to a concrete ring at the top and a concrete disc at the bottom in such a way as to leave an annular clearance. This annular space is used for collecting hydrogen and caustic. A diaphragm of asbestos paper, usually 0.06 inch thick, is placed on the inside of the perforated inner cylinder which forms the cathode. The anode arrangement consists of 24 sticks of graphite 2 inches square and 36 inches long, suspended in a circle from a concrete dome that closes the cell. The upper end of each graphite stick is machined to pass through holes in the concrete cover and threaded to take a lead nut. The upper ends of the graphite sticks are attached to a copper ring that distributes the current and is connected by copper cables to the cathode of the adjacent cell. Brine is fed to the cell through a chamber in which the brine stream is broken to minimize current loss; a float in the brine stream controls the brine level in the cells. This type of cell is normally operated with a constant voltage applied to the series circuit so that when the anodes and diaphragms are new, the cells operate at about 1500 amperes. After the anodes have worn, increasing the gap between the anode and the cathode, the operating current drops to about 1000 amperes. The cell utilizes an unsubmerged diaphragm so that initially the brine flow through the cell is high, gradually diminishing as the diaphragm ages. Consequently, the cell effluent contains about 85 grams per liter of caustic initially and up to 120 grams per liter near the end of the diaphragm life.

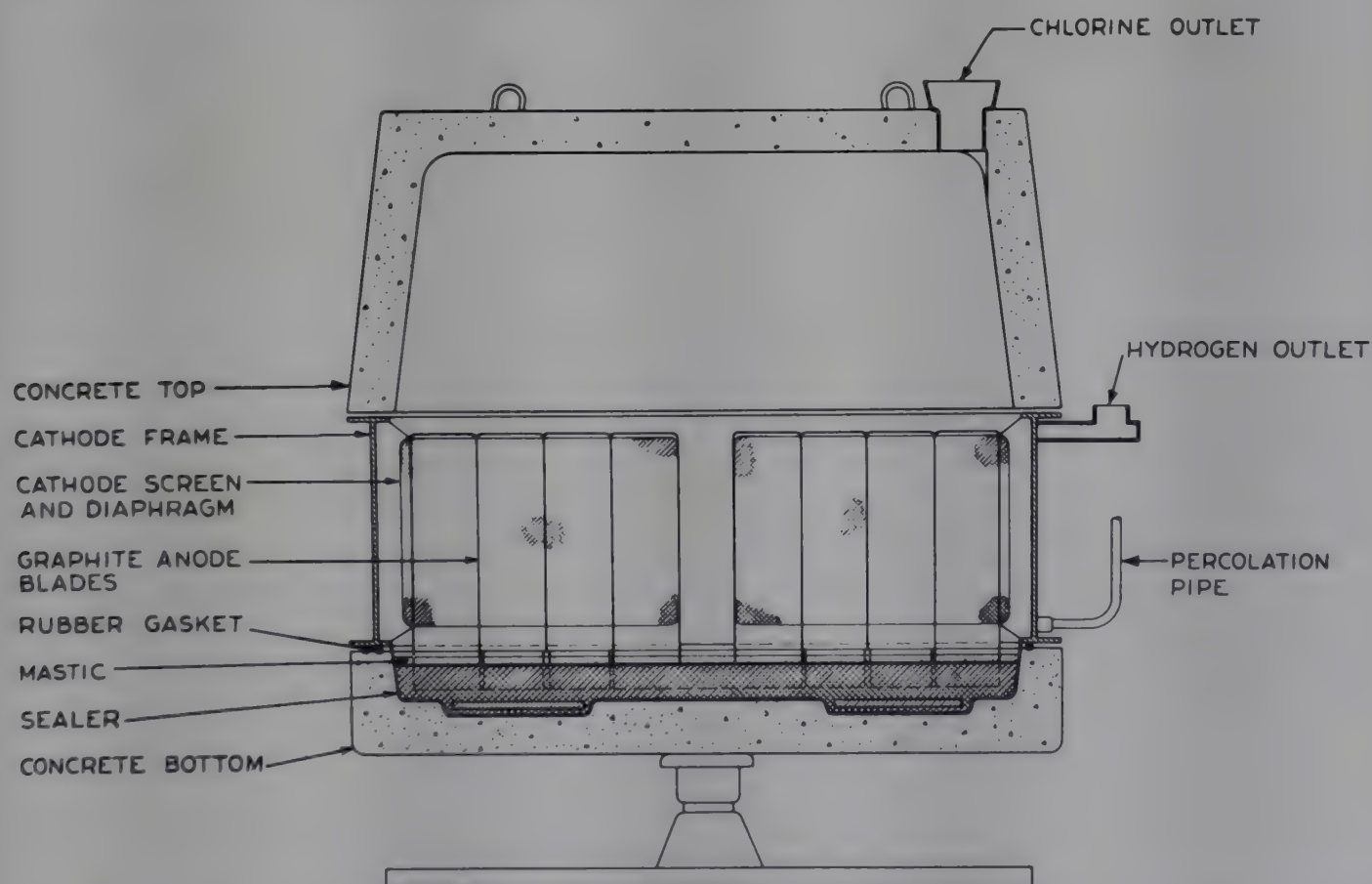


Fig. 9. Hooker Type S-3D, 40,000-ampere cell. Side sectional elevation. Courtesy Hooker Chemical Corporation.

Mercury Cathode Cells

In the mercury-cathode type of alkali-chlorine cell, continuously fed brine is partly decomposed in one compartment (called the electrolyzer) between a graphite anode and a moving mercury cathode, forming chlorine gas at the anode and sodium amalgam at the cathode. The sodium amalgam flows continuously to a second compartment, called the amalgam decomposer, secondary cell, or denuder, where it becomes the anode to a short-circuited iron or graphite cathode in an electrolyte of sodium hydroxide solution. Purified water is fed to the secondary cell, generally countercurrent to the sodium amalgam; hydrogen gas is formed, and the electrolyte increases in sodium hydroxide content. A solution containing from 30 to 70% sodium hydroxide at high purity overflows from the secondary cell. By far the largest number of mercury cells are operated to give 50% caustic soda strength. Purified and nearly saturated brine is fed to the cell and overflows at about 260 grams per liter of sodium chloride; it is generally freed of chlorine by vacuum, resaturated with dry salt, purified, and returned as fresh feed.

Sodium amalgam is formed in the electrolyzer because the overvoltage of hydrogen on mercury, as shown in Table 7, results in a discharge potential of hydrogen actually higher than that of sodium.

Table 7. Hydrogen Overvoltage of Several Cathode Materials in Dilute Sulfuric Acid at Room Temperature

Cathode material	Hydrogen overvoltage, volts, at current density	
	0.01 amp/cm ²	0.1 amp/cm ²
platinum black	0.04	0.07
platinum	0.07	0.29
iron	0.56	0.82
nickel	0.75	1.05
graphite	0.78	0.98
mercury	1.17	1.30

Most modern cells are constructed with a flat-bottomed steel trough. The mercury cathode flows uniformly over the flat bottom. Parts of the trough not in contact with mercury are provided with a corrosion-resisting protective coating such as hard rubber or, in one case, a high-quality granite stone. The bottom of the cell, which in operation is covered with a sheet of mercury, is in some cases bare steel, and in other cases hard rubber, granite, or concrete surfaced with a synthetic coating. Where covered bottoms are used, areas of bare steel are provided in order to have an electrical connection between the mercury cathode and the cathode bus bars. The anodes are usually horizontal graphite plates that hang on rods extending through the cover on the cell; either the rods are insulated from the cell cover or the cover itself is an insulator or is insulated from the steel trough which is at cathode potential. The anodes are parallel to and close to the mercury-brine interface and are perforated or grooved to facilitate release of chlorine. All modern cells are provided with a means of adjusting the space between the anode and the mercury surface while the cell is in operation, so that relatively high energy efficiency can be maintained throughout the life of the anodes. More recently considerable work has been done on the use of platinum-coated

titanium anodes which do not wear away as graphite does, thus maintaining permanently the optimum spacing between anode and cathode and eliminating the necessity for anode adjustment. A chlorine outlet is provided in the cover or else the chlorine passes out through an enlarged anolyte overflow connection.

There are two general types of amalgam decomposers. One consists of a horizontal steel trough mounted parallel to the electrolyzer, either beside or underneath it. Graphite grids are placed in the trough to serve as a cathode of the secondary cell. The other type is a vertical cylindrical steel vessel mounted close to the mercury outlet of the electrolyzer. The cylinder is packed with broken pieces of graphite over which the amalgam is distributed so that countercurrent flow with the purified water is obtained. The denuded mercury is collected in a small reservoir and recycled continuously to the main cell by a centrifugal pump mounted on each cell. In usual practice, the amalgam leaves the electrolyzer containing 0.2% sodium (by weight) and is returned with less than 0.02% sodium. The mercury cell has a fundamental disadvantage of about 0.9 volt compared to the diaphragm cell. This is partly compensated for because there is no diaphragm to impose a resistance and the electrodes can be set closer together. In practice, mercury cells are operated at two to six times the current density of diaphragm cells; nevertheless the voltage of mercury cells averages 0.6 volt higher than for diaphragm cells, the extremes ranging from about 0.4 to 1.0 volt.

The current efficiency of the mercury cell varies between 94 and 97%, which is about the same as for diaphragm cells. The energy requirement per unit of production is from 15 to 20% higher than for diaphragm cells because of the higher individual cell voltage requirement.

Similarly to diaphragm cells, the mercury cells require anode renewal, although on an average their consumption of graphite is slightly lower, but they do not require diaphragm renewal. On the other hand, the mercury must be continuously washed with pure water and certain parts of the cells must be periodically cleaned. A small mercury distillation unit is a necessary auxiliary to a mercury cell plant in order to recover the mercury contained in the sludge removed from the cells during the cleaning. Mercury cells also have the disadvantage of an unavoidable, although reducible, mercury consumption, which over a long period is of the order of 0.3 lb per ton of chlorine, ranging from 0.2 in well-operated installations to 0.5 or higher in others.

The following brief descriptions of some of the more important mercury cells now in use give an idea of the design concepts being employed.

BASF Cell. This cell has been developed and is built by Badische Anilin- und Soda-Fabrik A.G. at Ludwigshafen, Germany, in the 40,000-, 80,000-, and 120,000-ampere sizes. It differs from all other cells in having a one-piece, completely rubber-covered electrolyzer trough as well as a completely rubber-covered horizontal decomposer. The cathode connections are large, flat-headed bolts with heads slightly lower than the cell bottom so that they are always covered with mercury. The cell bottom is semirigid and the slope and flatness are adjusted by a multiplicity of leveling screws. The horizontal decomposer, containing graphite grids, is mounted beneath the electrolyzer to conserve floor space.

Solvay Cell. This cell, developed by Solvay et Cie of Brussels, is built in two sizes, one nominally rated at 96,000 amperes and the other at 160,000 amperes, and features a number of innovations not available on other cell types. The electrolyzer consists of a bare steel bottom with rubber-lined steel sides. The rubber-lined steel cell covers are in multiple sections mounted on wheels; the anodes are suspended

from these cover sections in such a manner that individual anode adjustment is possible. Contact to the anode stem is made through a tight slip-fit graphite sleeve. Spent anode assemblies are removed at one end of the cell and the remaining sectional anode assemblies are progressively advanced along the cell trough and new anode assemblies are added at the other end. Because of this feature, anodes can be replaced while the cell is in operation.

No walkways are required between cells because the top of the cell itself serves this purpose. The cell covers are sealed by means of 1-inch diameter, inflatable rubber tubes, eliminating the usual bolted or clamped gasketed joints between the cell cover and the cell trough.

The horizontal steel trough decomposer is located beneath the electrolyzer to conserve space. The mercury pump can be changed in a few minutes without stopping

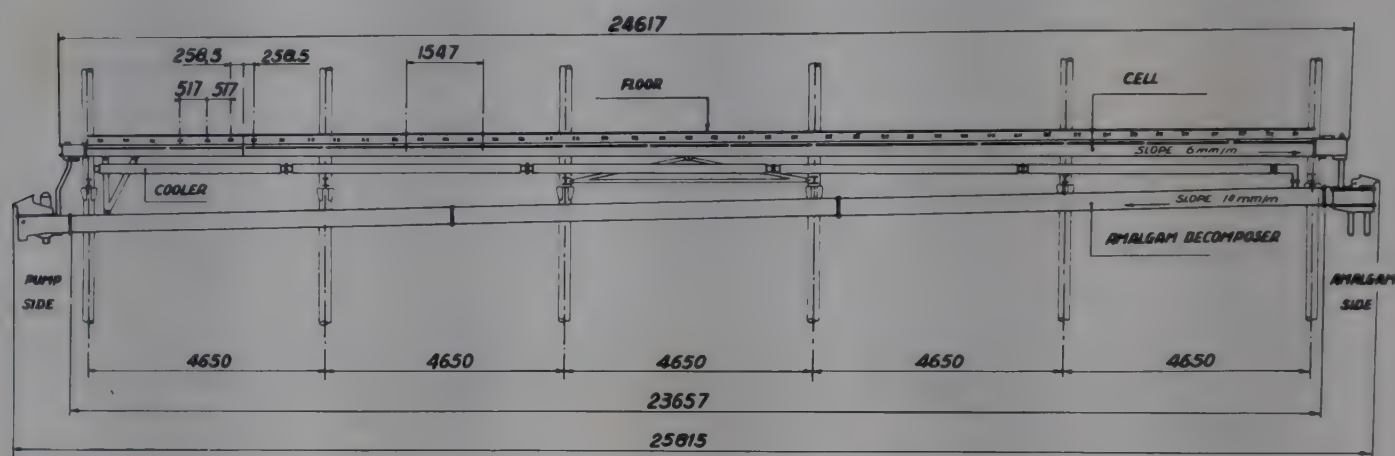


Fig. 10. Longitudinal section of a Solvay cell. Courtesy Electrochemical Processes Inc.

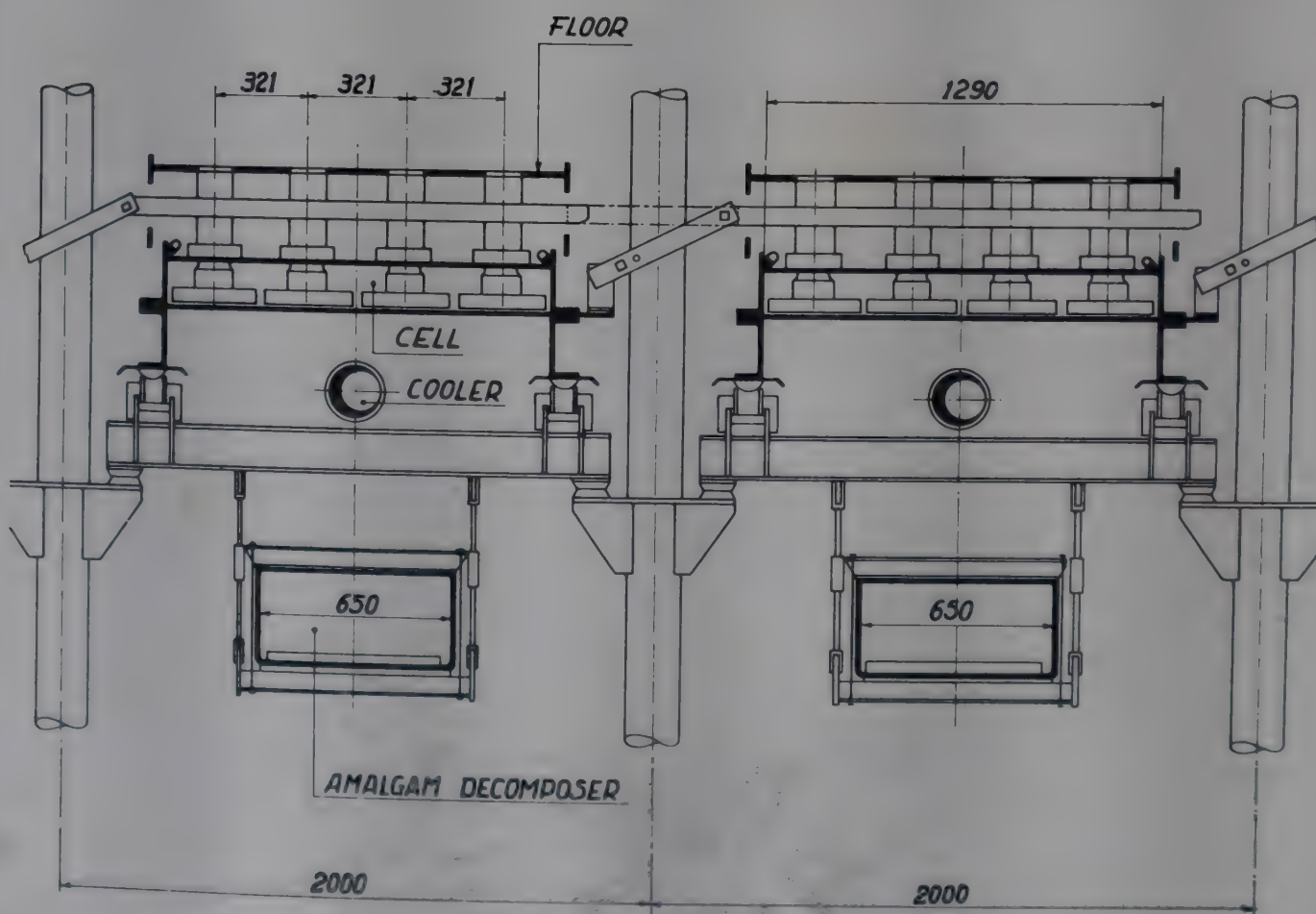


Fig. 11. Cross section of a Solvay cell. Courtesy Electrochemical Processes, Inc.

the cell. Because of the unique anode replacement method, no large capacity overhead cranes are required; therefore, these cells lend themselves to installation on two or four levels instead of the usual single level, thus conserving not only cell room floor space, but land as well. These cells are in use throughout the world by Solvay et Cie and in the U.S.A. by Solvay Process Division of Allied Chemical Corporation. Longitudinal and cross sections are shown in Figures 10 and 11 (dimensions in millimeters) and adjustment of the anodes in Figure 12.

Uhde Cell. These cells are manufactured in Germany by Friedrich Uhde G.m.b.H., Farbwerke Hoechst A.G., and Farben Fabriken Bayer A.G., the developers of the cell. They are presently being built in 5-, 10-, 20-, and 30-square-meter sizes rated nominally at 25,000, 50,000, 100,000, and 150,000 amperes. The electrolyzer uses an unlined steel bottom. The cover, side walls, and inlet and outlet compartments are rubber-lined. The bare steel bottom is of heavy construction with machined surface to maintain flatness. Individual anode adjustment is provided. The horizontal decomposer is constructed of unlined steel and contains graphite grids partially submerged in mercury. A cone-shaped centrifugal impeller serves as a pump for recycling the mercury to the electrolyzer. Figure 13 shows a cross section of the cell.

Pittsburgh Plate Glass Company and Hooker Chemical Corporation are using cells of this type in the U.S. These cells are also in use in Switzerland, France, Finland, England, India, Venezuela, Brazil, Australia, and, of course, Germany.



Fig. 12. Adjusting anodes of a Solvay cell. Courtesy Electrochemical Processes, Inc.

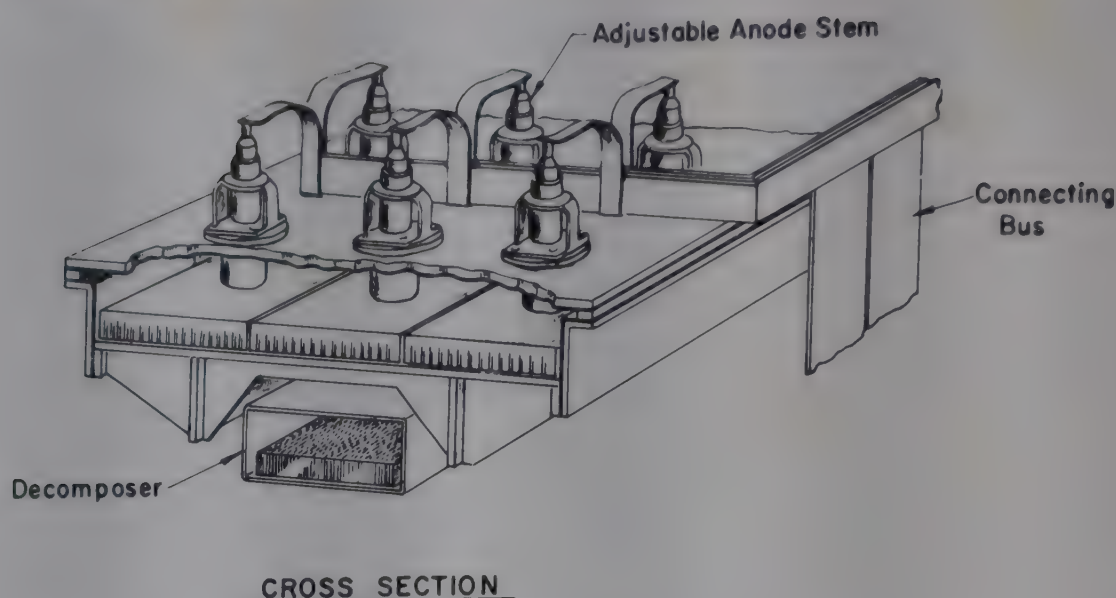


Fig. 13. The Uhde cell. Courtesy Hoechst-Uhde Corporation.

De Nora Cells. Oronzio de Nora Impianti Elettrochimici of Milan, Italy, has manufactured cells of many sizes and of continuously improved design for installation throughout the world. The de Nora cell design lends itself to considerable flexibility in operating conditions and possibly requires less meticulous control than most other types of mercury cells. De Nora cells are in operation in all the western European countries and on a worldwide basis—India, Iran, Egypt, United States, Canada, Mexico, Brazil, Argentina, Colombia, and Australia. A 60,000-ampere size and a 150,000-ampere size embody the 1960 improvements.

The electrolyzer consists of a steel trough with the sides and end boxes lined with a high-quality granite stone. The bottom is covered with concrete which is surfaced with a synthetic material resistant to chemical attack. Exposed longitudinally through the concrete bottom are the faces of steel T bars which serve as electrical contact between the mercury and the cathode leads. Bare steel bottom cells are also furnished by de Nora where a high-purity brine and skilled operators are available.

Graphite anodes are suspended from an outside steel frame by means of treated graphite rods and copper connections. This steel frame may easily be moved vertically in order to adjust the distance between anodes and the mercury cathode. The adjustment can be made during operation of the cell in such a way as to maintain minimum voltage.

A flexible rubber cover seals the top of the cell and permits anode adjustment. The rubber cover, with steel frame and anodes, can be turned 180 degrees (in the horizontal plane) to reverse the position of the anodes and thus obtain best utilization of graphite. The decomposer is a vertical, cylindrical welded-steel tower containing a basket packed with graphite lumps. A centrifugal pump recycles the mercury to the electrolyzer. The de Nora cell is shown in Figure 14.

Mathieson Cells. These cells have been developed by the Olin Mathieson Corporation and are primarily in use by that company. The model E-8, 30,000-ampere cell has been in use for about 10 years. The latest design, model E-11, rated at 100,000 amperes maximum, went into operation at Niagara Falls, New York, early in 1961, and in Charleston, Tennessee, early in 1962.

The electrolyzer consists of a bare steel plate bottom with hard-rubber-covered steel panels bolted on to form sides. The inlet and outlet end boxes are of cast iron



Fig. 14. The de Nora 150,000-ampere cell. Courtesy Oronzio de Nora Impianti Elettrochimici.

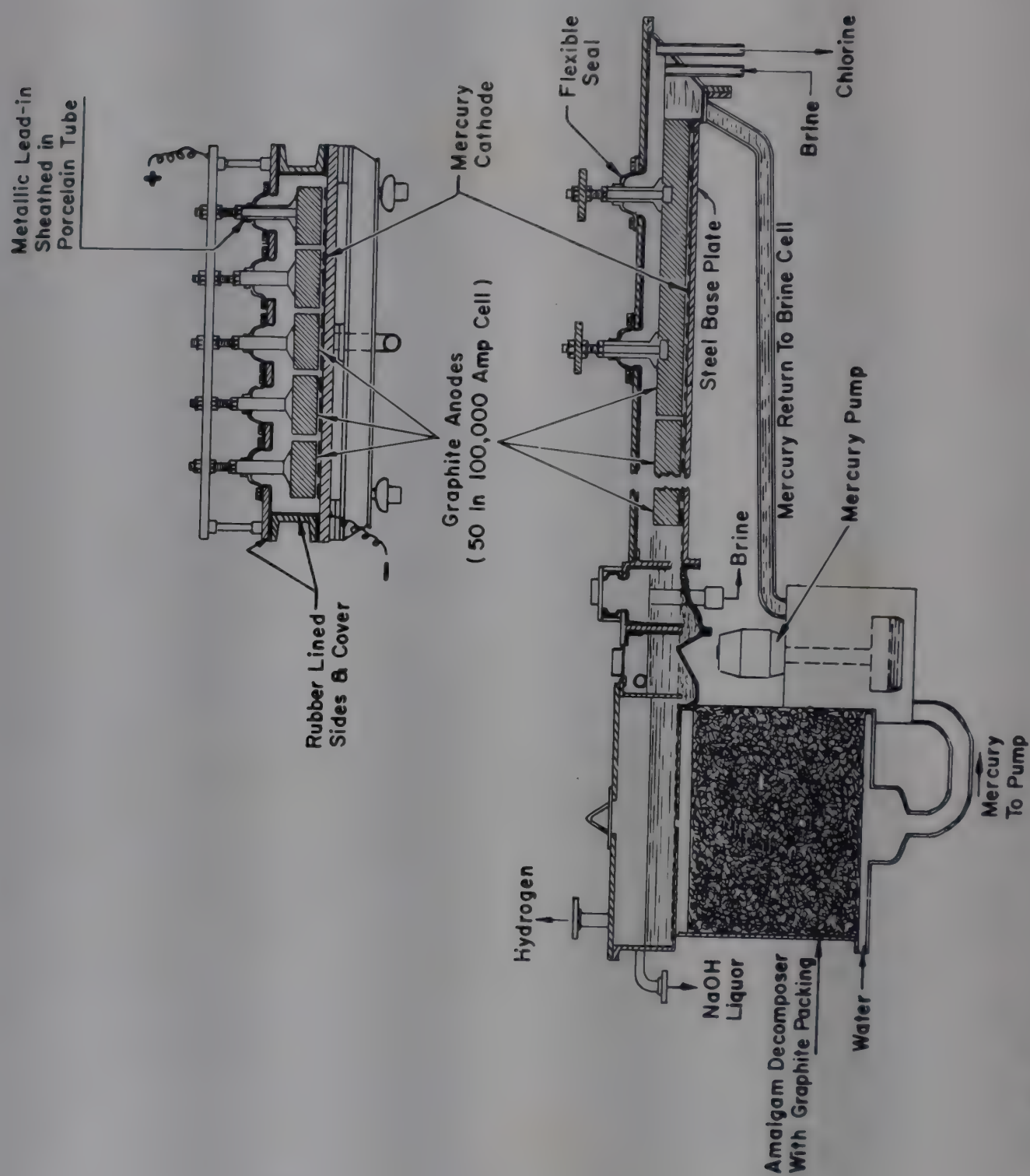


Fig. 15. Mathieson mercury cell diagram. Courtesy Olin Mathieson Chemical Corporation.

lined with hard rubber. The steel plate cover is lined with rubber on all surfaces exposed to chlorine. The cover rests on soft rubber gaskets and is clamped to the side panels and end boxes with C clamps, thus providing a gas-tight enclosure.

Fifty graphite anodes, each 4 in. \times 9 in. \times 48 in., are suspended from the distributing bus bars with two metallic lead-in posts per anode which are protected with porcelain sleeves. The lower surfaces of the anodes are slotted and holes are drilled into each slot from above to promote the flow of chlorine away from the active surface.

The decomposer is a vertical tower packed with lumps of broken graphite held between screens compressed by jack screws. The amalgam enters the top of the decomposer through a double seal and is distributed evenly over the top of the packing. Purified water enters the bottom of the decomposer below the packing and 50% sodium hydroxide overflows from above the packing. Hydrogen is piped from a connection on top of the decomposer. The denuded mercury collects in a well in the bottom of the decomposer and flows to a sump-type centrifugal pump for recirculation to the electrolyzer. (See Figs. 15 and 16.)

Technical data concerning all of the foregoing diaphragm and mercury cells have been assembled in Table 8. This table combines factors concerning the size, efficiency, and some of the technical bases for economic comparisons. (A comparison of economic data is given in Table 10, p. 698.)

Comparison of Mercury and Diaphragm Cells

Table 9 shows the installed chlorine capacity in the U.S. for both diaphragm and mercury cathode cells. In the U.S.A. in 1960, less than 20% of the installed capacity was mercury cathode cells. Installations under construction during 1962 would bring that fraction to just under 23%. However, the situation is quite different in other countries where the mercury cell accounts for a much larger percentage of the installed

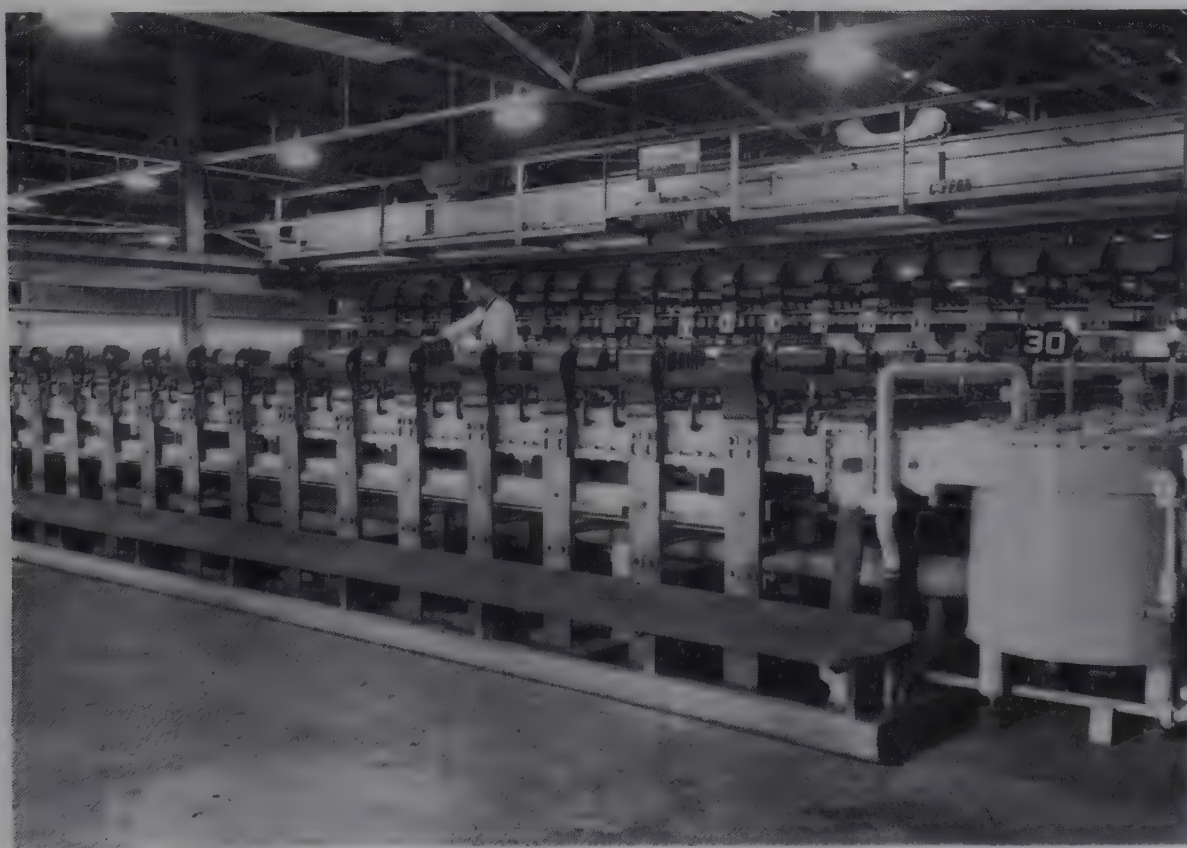


Fig. 16. A Mathieson mercury cell installation. Courtesy Olin Mathieson Chemical Corporation.

Table 8. Characteristics of Chlorine-Caustic Cells

Characteristic	Diaphragm cells				Mercury cells									
	Diamond		Hooker		BASF	De Nora		Mathieson		Solvay		Uhde		
	D-2	D-3	S	S-3B		14 X 3	18 X 6	E-8	E-11	V-100	V-200	10 m ²	20 m ²	
rated amperes	20,000	30,000	10,000	27,000	40,000	80,000	60,000	150,000	30,000	100,000	96,000	160,000	50,000	100,000
maximum amperes	24,000	37,000	13,000	30,000	50,000	100,000	80,000	200,000	34,000	110,000	110,000	190,000	60,000	120,000
cathode area, in. ²	30,800	44,200	18,700		17,900	35,600	18,522	48,084	9,650	23,200	28,000	46,500	15,500	31,000
cathode current density, amp/in. ²														
rated	0.648	0.68	0.535		2.23	2.24	3.23	3.15	3.10	4.30	3.43	3.45	3.22	3.22
maximum	0.78	0.77	0.697		2.80	2.81	4.32	4.26	3.53	4.74	3.93	4.08	3.87	3.87
av cell voltage, volts ^a														
at rating	3.78	3.82	3.75	3.85	4.25	4.25	4.30	4.30	4.50	4.43	4.34	4.34	4.25	4.25
at maximum	3.99	4.00	4.05	3.95	4.50	4.50	4.96	4.94	4.75	4.54	4.52	4.56	4.48	4.48
current efficiency based on NaOH, %	96.5	96.5	96	96	94-95	94-95	96-97	96-97	95	95	95	95	96-97	96-97
energy, dc, kw-hr/short ton of anode Cl ₂ ^a														
at rating	2,700	2,720	2,680	2,750	3,080	3,080	3,220	3,220	3,250	3,200	3,130	3,130	3,050	3,050
at maximum	2,840	2,840	2,900	2,820	3,260	3,260	3,500	3,490	3,430	3,300	3,243	3,280	3,210	3,210
graphite anode consumption, ideal conditions, lb/short ton Cl ₂	7.5	7.5	6.7	5.3	5.6	5.6	4.0-5.0	4.0-5.0	5.3	4.4	5.5±1	5.5±1	4.0	4.0
mercury consumption, lb/short ton Cl ₂					0.25-0.30	0.25-0.30	0.2-0.4	0.2-0.4	0.5	0.4	0.275	0.275	0.35	0.35
anode life, av days at rating	228	228	340	310	335-375	335-375	300	300	210	150	240	330	450	450
diaphragm life, av days at rating	110	110	113-170	103-155										
concentration of cathode alkali, % NaOH	11-11.5	11-11.5	10.9	11.5	50	50	50-55	50-55	50	50	55 max	55 max	50-63	50-63
chlorine production at rating, short tons/cell day	0.67	1.01	0.336	0.907	1.33	2.67	2.0	5.0	1.0	3.32	3.2	5.33	1.69	3.37
cell room area, ft ² /short ton day Cl ₂	140	105	226	96	285	228	190	155	215	104	167 ^b	138 ^b	217	147

^a Includes electrical connections.

^b Approximately half these areas when the cells are arranged on two levels.

Table 9. Installed United States Chlorine Capacity for Each Major Type of Cell in 1960

Manufacturer	Chlorine, tons/ day	Percent	
		Of sub- division	Of total
<i>Diaphragm cells</i>			
Columbia-Hooker	1,050	9.7	7.9
Diamond	1,215	11.2	9.1
Dow	1,685	15.5	12.6
Hooker	6,411	59.2	48.1
Vorce, Gibbs, Allen-Moore, etc	481	4.4	3.6
<i>total</i>	10,842	100.0	81.3
<i>Mercury cathode cells</i>			
Castner-Rocking	120	4.8	0.9
De Nora	817	32.9	6.2
Dow	100	4.0	0.8
Imperial Chemical Industries	224	9.0	1.7
Mathieson	525	21.1	3.9
Solvay	525	21.1	3.9
Hoechst-Udhe	160	6.4	1.2
Miscellaneous	17	0.7	0.1
<i>total</i>	2,488	100.0	18.7

capacity. Probably the most important reason for the difference between United States and foreign practice is that the raw material for most European and Japanese chlorine plants is solid salt rather than brine. Most chlorine plants outside the U.S.A. are auxiliaries to chemical plants, rather than centralized, high-efficiency operations as is the tendency in the United States.

The two most important factors governing the choice between mercury cathode and diaphragm cells are the physical form in which salt is available and the quality of the caustic required by the market or end use. Because of the water balance, the mercury cell requires dry salt. Diaphragm cells are normally operated on saturated brine. Dry salt costs four to eight times as much as salt in well brine. In general, diaphragm cells are more economical where operation is located near a source of deep-well, saturated brine. There is an advantageous combination of mercury and diaphragm processes which is used in a number of plants. The diaphragm cells are supplied with saturated brine, and the mercury cells are supplied with dry salt obtained from the concentration of the diaphragm cell caustic.

The mercury cell process produces a superior quality caustic at 50% NaOH concentration directly from the cell assembly by the decomposition of the mercury-sodium amalgam with good quality water (see Table 2, p. 755). The diaphragm cell produces a weak caustic liquor containing about 10% caustic and 15% unconverted salt. During the concentration of the weak cell liquor, most of the salt is precipitated, filtered from the caustic, and recycled. The resulting caustic contains about 1% salt on a 50% caustic basis, plus the small amount of sodium chlorate generated in the diaphragm cell.

The rayon industry demands a low-salt, low-chlorate caustic, and it tolerates minor impurities only if their concentration is held between narrow limits. Therefore purification of diaphragm caustic with liquid ammonia extraction is usually practiced, and if the major market for any one installation is the viscose rayon industry, the

mercury cell is favored. Diaphragm caustic, as concentrated to 50%, with the usual 1% NaCl, is quite satisfactory for refining of petroleum, manufacture of alumina, soaps and detergents, phenol, and other general uses.

An economic factor frequently overlooked in comparing the two processes is the U.S. Treasury Department's ruling that the mercury inventory is a nondepreciable asset. The mercury inventory will vary from under 2000 lb of mercury per ton per day of chlorine capacity in the larger cells, to over 3000 lb per ton per day in the smaller installations. Hence some 10 to 15% of the total investment is nondepreciating.

The mercury cell has some advantage over the diaphragm cell in flexibility of capacity adjustment. The diaphragm cell is best as a baseload piece of equipment, as frequent capacity variation tends to deteriorate the diaphragm. This capacity flexibility of the mercury cell lends itself to utilization of off-peak power, where such power is available. However, most chlorine plants are provided with storage and the demand is scheduled so as to give a uniform rate of production over long periods of time. Table 10 gives an economic comparison of mercury and diaphragm cell plants. The unit figures are total consumption (chlorine plus caustic) based on chlorine only.

Table 10. Economic Comparison of Chlor-Alkali Plants
(Approximate values for average plant size in 1960)

Factor	Mercury cathode cells	Diaphragm cells
salt consumption, tons NaCl/ton Cl ₂	1.7	1.8
salt, physical form	dry	saturated brine
fuel consumption, millions of Btu/ton Cl ₂		
for making salt from brine	4.0	
for caustic concentration		4.0
electric power (electrolysis only), kw-hr/ton Cl ₂	3,200	2,700
graphite consumption, lb/ton Cl ₂	5 to 7	6 to 8
mercury consumption, lb/ton Cl ₂	0.4 to 0.5	
asbestos consumption, lb/ton Cl ₂		1.20
cell room maintenance labor, man-hr/ton Cl ₂	0.32	0.29
volts per cell	4.5	3.8
current density, amp/in. ² cathode	3.8	0.7
area cell room floor in ft ² /daily ton Cl ₂	200	110
health hazard	requires caution	normal industrial
investment, 1960 \$/daily ton Cl ₂	94,000	87,000

Chlorine Plant Auxiliaries

The auxiliary facilities for a diaphragm cell plant (Fig. 17) consist of brine purification; direct-current electric power supply; chlorine cooling, drying, and liquefaction; caustic evaporation; salt recovery; caustic cooling and filtering; and when utilized, hydrogen cooling and compression. Similar facilities are required in a mercury cell plant except that brine treatment requirements are somewhat different and caustic evaporation and salt recovery facilities are not required. (See Fig. 18.)

Brine Purification. All common salt, being contaminated with calcium, magnesium, and other undesirable elements, must be purified before it can be used satisfactorily in chlorine cells. Mercury cell installations require resaturation of the anolyte with solid salt and this is usually followed by purification. Other plants

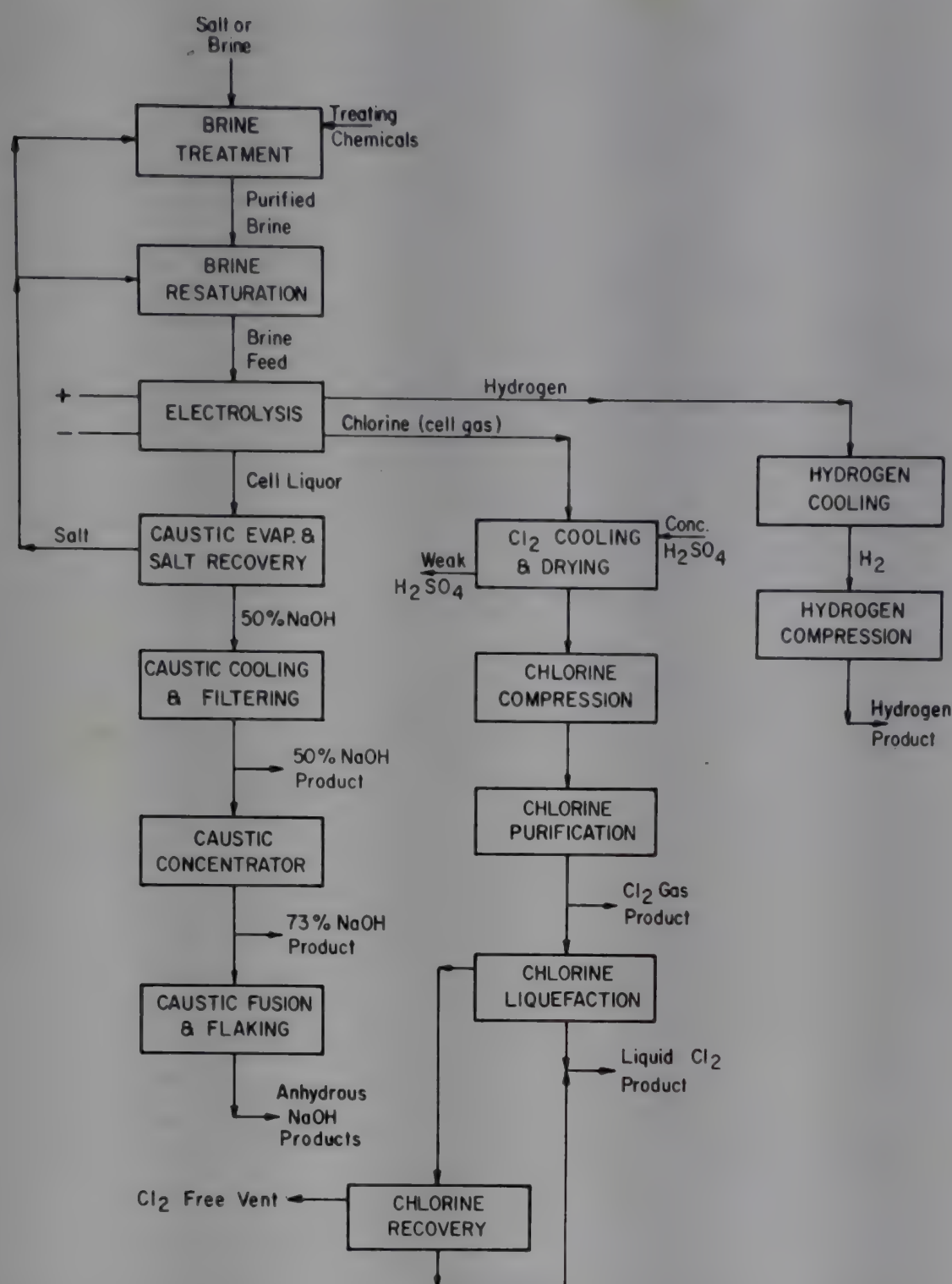


Fig. 17. Flow diagram of diaphragm cell operation in a chlorine-caustic plant.

dissolve solid salt in water, or obtain salt as brine from deep rock salt wells. Where solid salt is used, it may be either mined rock salt from some underground deposit, or from evaporation of natural brines or sea water. Solar evaporation is used to a large extent for recovery of solid salt from sea water.

In diaphragm cell plants, brine, obtained from deep wells or by dissolving solid salt with fresh water, is usually treated with sodium carbonate and calcium or sodium hydroxide to precipitate calcium and magnesium, respectively. In most installations the precipitate is removed in flocculating-type settlers. In some cases, however, the treatment is carried out at elevated temperatures which promote more rapid reaction and a faster settling precipitate, thus minimizing the need for large-diameter settlers. Barium chloride and barium carbonate are sometimes used for reducing the sulfate concentration in the brine. Where the cost of these chemicals is high or the cost of

To reduce to a minimum the amount of diaphragm plugging or the amount of cleaning required in mercury cells, the brine being fed is filtered after treatment. In some cases the sodium carbonate required for treatment is obtained by the carbonation of caustic soda using flue gas.

Direct-Current Electric Power Supply. The satisfactory operation of chlorine cells requires a dependable source of direct-current electrical energy from high-efficiency rectifiers. In most cases this is accomplished by converting available alternating-current power to direct current by the use of motor generator sets, rotary converters, mercury arc rectifiers, or, more recently, by mechanical contact rectifiers and semiconductor rectifiers using germanium or silicon diodes. Until the development of mechanical rectifiers and semiconductor rectifiers it was necessary to go to relatively high dc voltages in order to obtain high conversion efficiency. With the new developments this is no longer necessary. Consequently, the trend is to install chlorine cells utilizing much higher current and, as a result, a smaller number of cells in series, thereby simplifying cell room operation and reducing maintenance costs by installing fewer units.

Semiconductor rectifiers are rapidly gaining favor over mechanical-contact rectifiers because of their much greater simplicity, which results in lower investment costs and less maintenance. (See Semiconductors.)

Chlorine Cooling, Drying, and Liquefaction. Chlorine gas emerging from cells is collected in manifolds, generally of stoneware, polyvinyl chloride, or other synthetic material, under a precisely controlled slight vacuum. This gas usually contains, in addition to the water vapor in equilibrium with it, fine sprays of brine, some carbon dioxide from anode deterioration, the diluent air sucked in at the various points of small leakage, and the hydrogen from diaphragm diffusion, or from amalgam anolyte reaction. Most of the water vapor is separated by cooling the chlorine gas, either in a direct-contact water scrubber (to the limit of chlorine hydrate formation, in the neighborhood of 56°F), or by contact with stoneware, titanium, or glass pipes, through which cooling water is circulated. Most of the brine mist separates out in the same operation. The gas is next dried with sulfuric acid. This is usually done in a series of towers where acid flows countercurrent to chlorine gas. The acid, at 90 to 100% concentration, starts into the last (with respect to the chlorine gas flow) of several towers, or sections of towers, in series—usually three or four—and is discarded at about 60% strength at the outlet of the first tower or tower section. If the gas is cooled to about 20°C, the amount of sulfuric acid used is about 25 lb per ton of chlorine, and the dried chlorine contains less than 0.5 mg of water per liter. The unseparated salt spray forms sodium sulfates in the chlorine drying towers and is a cause of some trouble in the equipment beyond. For that reason many chlorine plants have a special fume catcher or dust separator of glass wool filters, or the like.

Compression of the chlorine gas is accomplished by the use of sulfuric acid-lubricated reciprocating compressors; sulfuric acid-sealed rotary compressors, such as Nash Hytors; nonlubricated reciprocating compressors; and centrifugal compressors or blowers. Preference has been shown for reciprocating compressors in Europe and for rotaries in the U.S.A. However, the general trend is toward centrifugal compressors and greater utilization of nonlubricated reciprocating compressors. Carbon piston rings, or carbon cylinder liners, are usually used in the nonlubricated reciprocating compressors, other parts being cast iron. Centrifugal compressors become economical only in the larger chlorine plants (200 ton-per-day capacity and

up). Precise control of the cell room manifold pressure is usually maintained either with a bypass control valve to bleed some of the compressed chlorine back into the suction, or by a throttling butterfly valve in the compressor suction line. The suction at the compressor is usually of the order of 5 or 6 inches of water to take care of the pressure drop through coolers and dryers. The discharge pressure for which an installation is designed may range from 20 to 150 psia, depending upon the type of compressors being used and upon the temperature to which the chlorine is to be cooled for liquefaction. In operation, the discharge pressure is controlled by the rate at which noncondensables are purged.

The compressed chlorine gas passes through separators to remove most of the entrained sulfuric acid and then, in some cases, particularly in diaphragm cell plants, to a chlorine purification unit where the chlorine gas is washed with liquid chlorine, usually in a packed tower, to remove the low-boiling organic materials.

Hydrogen Cooling and Compression. The hydrogen gas produced from either the diaphragm or mercury-cathode type of chlorine cell has a relatively high purity and requires very little processing to make it suitable for most commercial utilizations. From diaphragm cells the gas is collected in steel headers and cooled by direct-contact cooling towers. The scrubbing action thus obtained also removes the minor quantities of entrained caustic soda. The gas is then compressed by the use of positive displacement compressors of conventional design such as water-sealed rotary compressors and reciprocating compressors. Depending upon customer requirements, the gas may be further dried by refrigerated cooling and other standard forms of dryers. Any oxygen present from minor air leakage can be removed by the use of Deoxo equipment using a nickel platinum catalyst.

Hydrogen from mercury cathode cells can be handled in much the same manner except that the initial cooling is usually performed in surface heat exchangers in order more completely to recapture mercury that is condensed in these units. Here again refrigerated cooling is frequently used not only to remove additional water vapor, but also to remove additional small amounts of mercury. Removal of the last traces of mercury is sometimes required and this is done by proprietary methods.

The other auxiliaries to a chlorine plant—those having to do with caustic soda evaporation and sodium chloride recovery—are described under Sodium hydroxide, p. 740.

Other Processes for Producing Chlorine

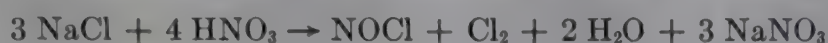
Potassium Chloride Electrolysis. A saturated potassium chloride solution can be fed to and electrolyzed in any of the cells that have been described. There is an unfavorable difference in the theoretical decomposition voltage which, however, does not always appear in diaphragm cell practice. Certain types of asbestos swell less in potassium than in sodium salt solutions, and this frequently more than neutralizes the voltage differences. Control instruments must, of course, be adjusted to the different solution densities, but in substantially all other respects the operations are identical.

Magnesium Metal Electrolysis. This process no longer puts any chlorine on the market. In fact, it has become a consumer in that chlorine is used for final dehydration of the magnesium chloride-fused salt.

Chlorine from Sodium Metal Production. Sodium metal is obtained almost exclusively from the electrolysis of fused sodium chloride using the Downs cell (see

Sodium). This cell produces hot and concentrated dry chlorine, which in most plants is cooled and liquefied as described under Chlorine plant auxiliaries. A cell, using a molten lead cathode, was being piloted in Japan during mid-1962.

Chlorine from Salt and Nitric Acid. The commercial production of chlorine by the interaction of salt and nitric acid, called the nitrosyl chloride process, is now more than a quarter of a century old, but is still practiced in only a single plant operated by the Nitrogen Division of Allied Chemical Corporation at Hopewell, Virginia. Of the several processes proposed to produce chlorine from salt without coproduct caustic (and also given some pilot plant development), the one practiced at Hopewell showed the most promise because of the ready market for sodium nitrate as a fertilizer salt. The first stage of the reaction can be represented by the overall equation,

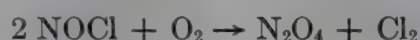


The nitrosyl chloride is separated from the product chlorine and treated with soda ash.



The salt is recycled, and the nitric oxide is used to prepare either nitric acid or sodium nitrate.

However, changes in fertilizer demands have resulted in a decline of sodium nitrate as a fertilizer outlet; ammonium nitrate has largely taken its place. This factor, taken with the corrosion difficulties of the process, has probably been the principal cause of the limited industrial development. The process has received some additional impetus in recent years in that the nitrosyl chloride can be oxidized (using 95% oxygen gas) to produce nitrogen tetroxide and elemental chlorine rather than sodium nitrate and common salt as in the original process.



Nitrogen tetroxide has been selected by the U.S. Air Force as the storable liquid oxidizer for the Titan II missile. However, the total 1962 chlorine capacity by this process was 90 short tons per day in a single factory, or about the same as at the end of World War II. In spite of the many places where both cheap nitric acid and cheap common salt are available, no other operator has shown sufficient interest in the process to build other facilities. A 1962 development of potential interest is the construction at Vicksburg, Miss., of a plant to convert KCl to KNO_3 —a valuable double fertilizer especially appropriate for use in underdeveloped countries. For a further discussion of this process see reference 8 (see also Table 3, p. 677).

Chlorine from Hydrogen Chloride or Hydrochloric Acid. The continually increasing production of hydrogen chloride from chlorination processes (solvents, synthetic resins, etc) has prompted renewed attacks on the problem of regenerating chlorine from HCl. The Oppau-Deacon process of I. G. Farben showed some promise in the operation of a 10-ton-per-day pilot plant toward the end of World War II. The Royal Dutch Shell (15-17) organization has developed and is prepared to license a process in which the Deacon type of oxidation of HCl is carried out with a new catalyst, the feature of which is the ratio of rare earth metals to copper (supported on silica gel) of at least 1:10. The Hercules Powder Company at Brunswick, Georgia, built and operated a 25-ton-per-day plant based on the Grosvenor-Miller variation of the Oppau catalyst. This plant was shut down before 1960 and had not resumed operations as of mid-1962.

Equipment for the electrolysis of hydrogen chloride is being developed by both de

Nora of Italy (18) and Uhde. Monsanto Chemicals at Anniston, Alabama, and elsewhere has undertaken further development of the de Nora process in the U.S.A.

Institut Française du Pétrole (16,19,20) of France has developed a process in which the oxidation of HCl is carried out by concentrated nitric acid which is in recycle; ordinary sulfuric acid concentration is required at temperatures on the order of 175°F.

The electrolysis of NiCl_2 (made by subjecting recycled metallic nickel to the attack of HCl) has been postulated to necessitate about the same capital (\$25,000 per daily ton of Cl_2) as the de Nora or Uhde electrolytic HCl plants, but only some 1350 kw-hr per ton as compared to the 1800 or so for the other processes.

The predictions of capital costs and operating costs appearing in the 1962 technical press give no clear indications as to where these several undeveloped processes are likely to find best application.

Health and Safety Hazards

Chlorine in General. Chlorine gas is primarily a respiratory irritant producing no permanent or cumulative effect for short exposures at "stinking" concentrations, or long exposures at undetectable concentrations. Neither liquid nor gaseous chlorine is a systemic poison. A well-documented case is the Brooklyn subway accident of June 1, 1944 (9). Over 1000 people were exposed with no evidence of lasting injury.

When sufficient concentration of chlorine gas is present, it will irritate the respiratory system and skin. Large amounts cause irritation of eyes, coughing, and labored breathing. Preventive health measures and first aid procedures are given in the Chlorine Institute's *Chlorine Manual* (10). Chlorine is not a serious industrial hazard if workers are adequately instructed in proper procedures. Good practice requires that suitable gas masks be available to every employee who handles chlorine. Emergency water showers and eye baths should be placed in convenient locations wherever chlorine is used.

The physiological response to various concentrations of chlorine gas is as follows (11):

<i>Effect</i>	<i>Parts of chlorine/million parts of air (volume)</i>
least amount required to produce slight symptoms after several hours exposure	1
least detectable odor	3.5
maximum amount that can be inhaled for one hour without serious disturbances	4
least amount required to cause irritation of throat	15.1
least amount required to cause coughing	30.2
amount dangerous in 30 minutes to 1 hour	40-60
kills most animals in very short time	1,000

Mercury Cell Installations. The large quantities of mercury being circulated in a mercury cell plant, plus the elevated operating temperature of the process, present a health hazard which requires specialized equipment design and copious cell room ventilation. Mercury is a systemic poison and continued exposure may result in cumulative effects. It is well-known that mercury can be absorbed through the respiratory tract by inhalation of vapor, or through the skin in contact with the liquid

phase. The most prominent symptoms of mercury poisoning are the psychic disturbance known as erethism (a peculiar form of timidity), tremor, pallor, and stomatitis manifested by salivation and tenderness of the gums. Conservative health authorities recommend a threshold average, for eight hours daily exposure, of 0.1 mg of mercury vapor per cubic meter of air.

To control the mercury vapor hazard in a mercury cell room, it is necessary to have the entire mercury circuit sealed vaportight. Merely covering the mercury body with water or salt brine is not adequate. The entire cell room must be well-ventilated, with air turnover several times the rate normal for a diaphragm cell installation. Maintenance of the equipment, disposal of parts that have been in contact with mercury, and mercury spillage require cautious handling. There are cases where employees experienced acute mercury intoxication from welding of metal parts that had been removed from the cell mercury circuit some time before the welding took place.

It is the experience of the industry that mercury poisoning can be prevented by proper design of the equipment, adequate ventilation, and careful attention to maintenance. It is recommended that frequent air traverse samples be taken and that any contamination be traced to its source. (For further information see references 12-14.)

Uses and Future Prospects of Chlorine

Chlorine, which was originally used almost entirely for bleaching, is no longer of great importance in this field. In fact, the textile bleaching uses of chlorine have dropped from about 10% of the total in 1930 to hardly more than 0.5% in 1960. Chlorine is too destructive for bleaching wool, silk, and other products of animal origin, and in recent years hydrogen peroxide has become economically available for these and other purposes.

Chlorine's fastest growing use is in the synthesis of chemicals, mostly in the organic chemical field. Such uses have increased from about 25% in 1930 to approximately 80% in 1960. The tonnage values corresponding to these fractions are

Table 11. Chlorine Consumption in the U.S.A.
(in thousands of 2,000-lb tons/year)

Category	1930	1940	1950	1960
solvents	22	93	423	676
automotive antifreeze and antiknock compounds	16	100	301	576
plastics, resins, and elastomers		20	128	497
pesticides		8	159	267
refrigeration fluids and dispersion propellents		5	71	226
inorganic compounds and metallurgical uses	4	46	208	385
organic intermediates not separately shown	9	64	255	736
other chemical uses	1	4	78	347
total	52	340	1,623	3,710
total of above	52	340	1,623	3,710
pulp and paper manufacture	95	170	315	740
textile bleaching	20	35	40	30
sanitation (water supply and sewage treatment)	30	50	90	155
net exports	4	5	8	1
total consumptions	201	600	2,076	4,636

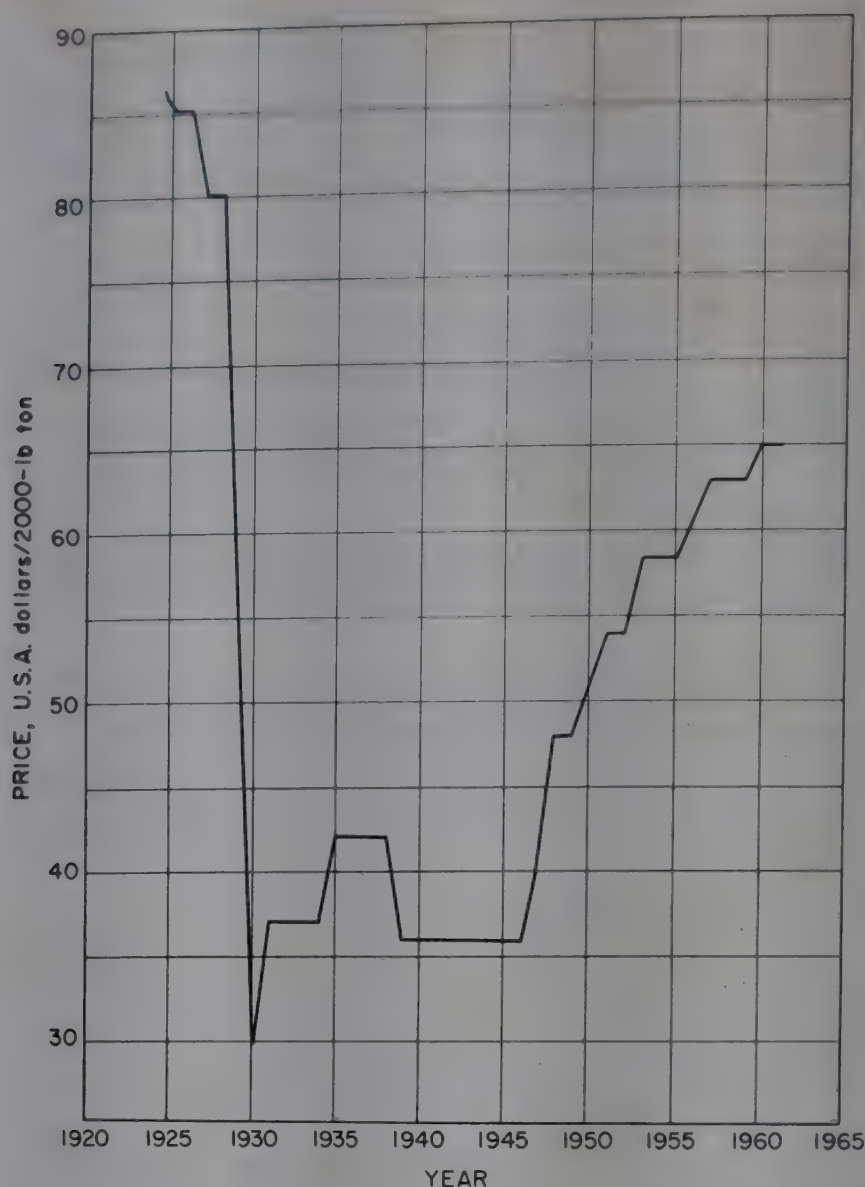


Fig. 19. United States chlorine prices in tank car lots.

even more impressive, as illustrated in Table 11. The trend in chlorine prices over the last four decades is shown in Figure 19.

In other countries, especially those of less advanced industrialization, the uses of chlorine in the fields of sanitation are proportionately much more important than in the U.S.A.

Over the thirty years summarized in Table 11, there have been several changes in the conventions and customs of reporting uses in several of the categories. Consequently, as the uses have proliferated, ambiguities have appeared. For example, some of the cyclopentadiene derivatives reported above among the "organic intermediates" might at times have been classed as solvents and pesticides by some writers on this subject.

The metallurgical uses of chlorine include several important methods not only of beneficiating ores and fluxing, but also methods for the actual extraction of copper, lead, zinc, nickel, gold, platinum, rare earth metals, titanium, tungsten, vanadium, and others.

The ultimate consumer products from many of the categories of Table 11 are as varied as clothing, jewelry, paints, foods, reading matter, tires, and toys. With such an extremely diversified market, and such a consistent record of accelerating growth, the chlorine industry tries to anticipate its future demands in forecasts in individual fields of use, as well as in the overall picture. As of 1962, the prospects are bright for

the immediate future, although there is clear and unmistakable evidence of a reduced rate of growth which will be noticeable during the 1970's.

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SODIUM CARBONATE

Sodium carbonate, Na_2CO_3 , formula weight 106, is a white, crystalline, hygroscopic powder. In chemical trade the terms "ash," "soda ash," "soda," and "calcined soda" are used for the anhydrous salt although soda ash is the most common name in English-speaking countries. In European countries and in some rural districts of the U.S.A., the word "soda" refers to the decahydrate as packaged for household use, but this commodity and the monohydrate have only minor commerce in comparison with the anhydrous forms. (See also Sodium compounds.) Sodium carbonate is moderately soluble in cold water and soluble to approximately 30% of solution weight in

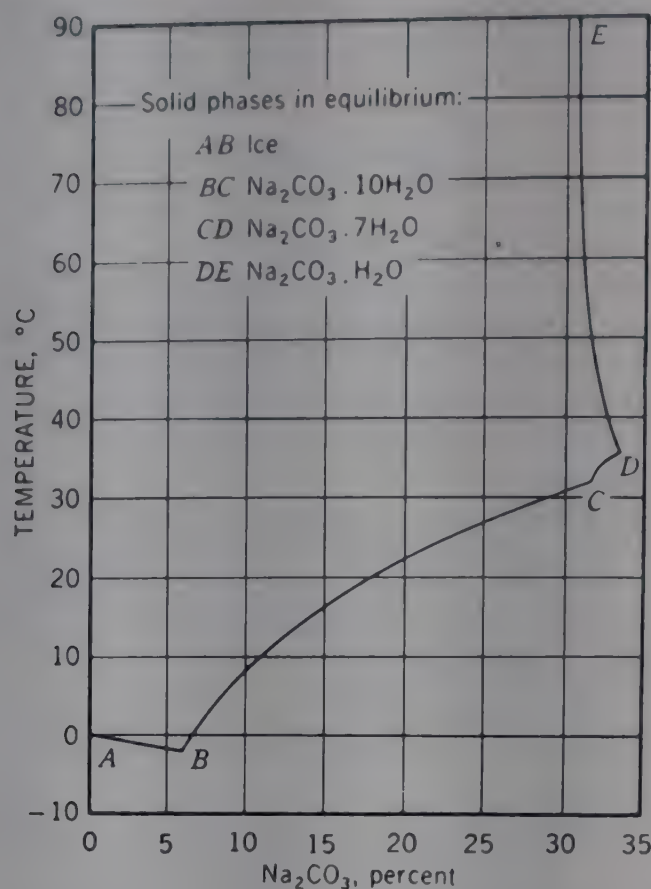


Fig. 1. Freezing point-solubility for system $\text{Na}_2\text{CO}_3\text{-H}_2\text{O}$ (1).

hot water (see Fig. 1); the solution is strongly alkaline because of hydrolysis. Melting point, 851°C ; heat capacity at 25°C , $26.41 \text{ cal}/(^\circ\text{C})(\text{mole})$; heat of fusion, 8 kg-cal/mole ; density at 20°C , 2.533 g/cm^3 . Bulk densities, in lb/ft^3 , of various commercial grades are as follows:

extra light ash.....	20 to 24 (no longer made)
light (or ordinary) ash.....	32 to 35
medium (or coarse light) ash (calcined trona).....	50 to 60
dense (granular or heavy) ash.....	62 to 67

In chemical commerce soda ash is almost synonymous with the term alkali. It is the most available high-tonnage, low-cost, reasonably pure, soluble alkali in today's traffic in chemicals. In these qualifications only ammonia offers soda ash a remote threat. Soda ash (and NaOH) are the sources of sodium from which practically all sodium compounds are prepared. The only cheaper bulk sodium compound is common salt which, even in the commercially refined state, is not so pure as soda ash. The biggest single use of soda ash is in the manufacture of glass which, in the U.S.A. in 1930, accounted for not much more than one-fourth of the total. As of 1960, despite the many new competitors of glass, especially in the container field, glass accounts for one-third of the soda ash used. Large amounts are consumed in the preparation of pure alumina (from bauxite) and sodium silicates for adhesive and catalyst manufacture. In Europe it was used in the "lime soap" processes, but this use is declining in favor of caustic soda. Soda ash is also used in water softening, textile processing, welding fluxes, flotation, desulfurization of iron and steel, and manufacture of pulp and paper. The direct use in soap manufacture in the U.S.A. has almost disappeared, but the new uses in phosphatic detergents have more than compensated. Figure 2 shows that during the last 30 years there has been a substantial reduc-

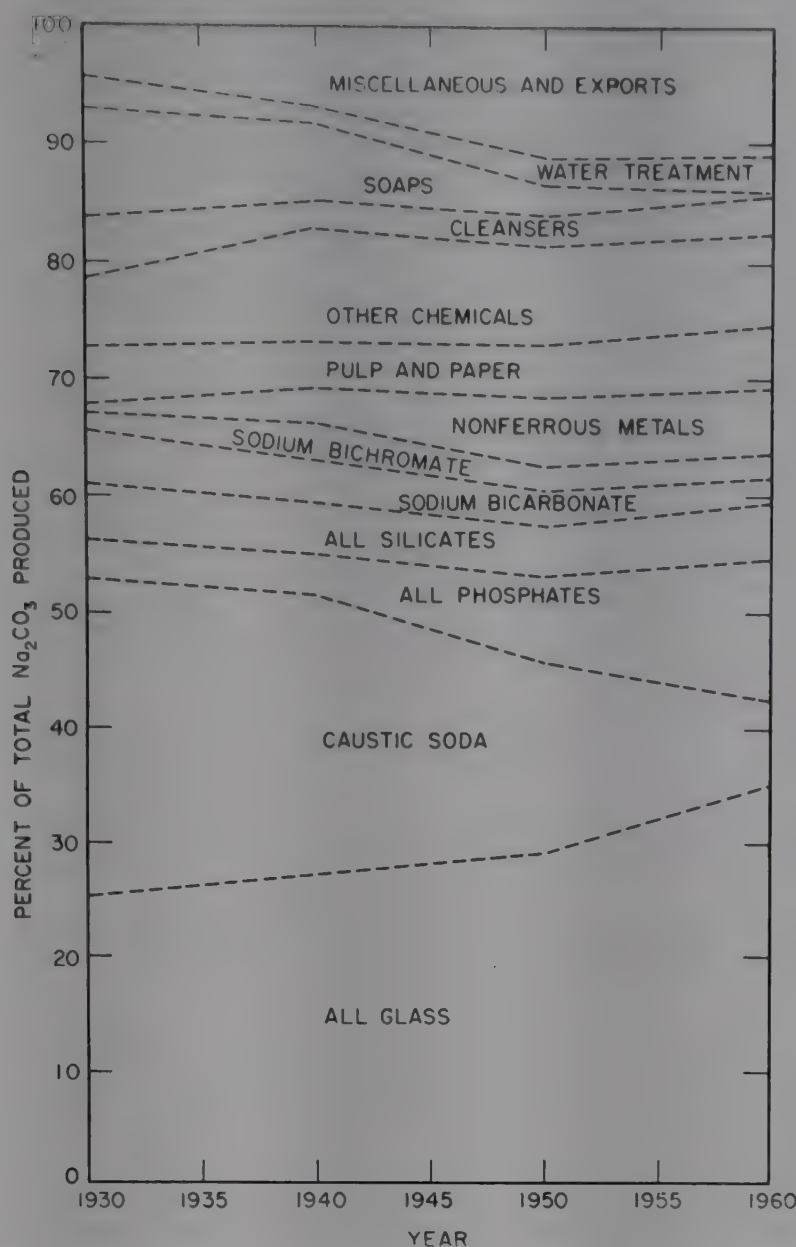


Fig. 2. Trends of soda ash uses in the United States.

tion in use of soda ash for conversion to caustic soda, but several increases—notably in sodium phosphates, aluminum, and “chemicals”—have concurrently taken place.

The original (Leblanc) process for synthetic manufacture of soda ash from salt was never used in the United States and was abandoned in Europe early in the twentieth century. The modern method is known as the Solvay process, which, although more than 100 years old, still produces some 15 million tons annually in the 70-odd factories of the world. The expansion of the Solvay process in industrialized countries is limited because of the rapid rise of the electrolytic process and greater exploitation of deposits of natural soda. Figure 3 shows the changes in the soda ash production methods for the world as a whole for the past 120 years.

The modern alkali factory is worthy of study not only because of its importance in chemical industry, but because during its long history it was an important contributor to the development of a number of basic chemical engineering techniques. The alkali manufacturer quarries a heavy stone and mines a deep mineral, and then transports the two to an expensive factory in which he processes them to produce an exceptionally pure and uniform bulk product (see Table 1) which reaches consumers' plants at a cost of approximately 2 cents per pound—almost as cheaply as domestic fuels reach consumers.

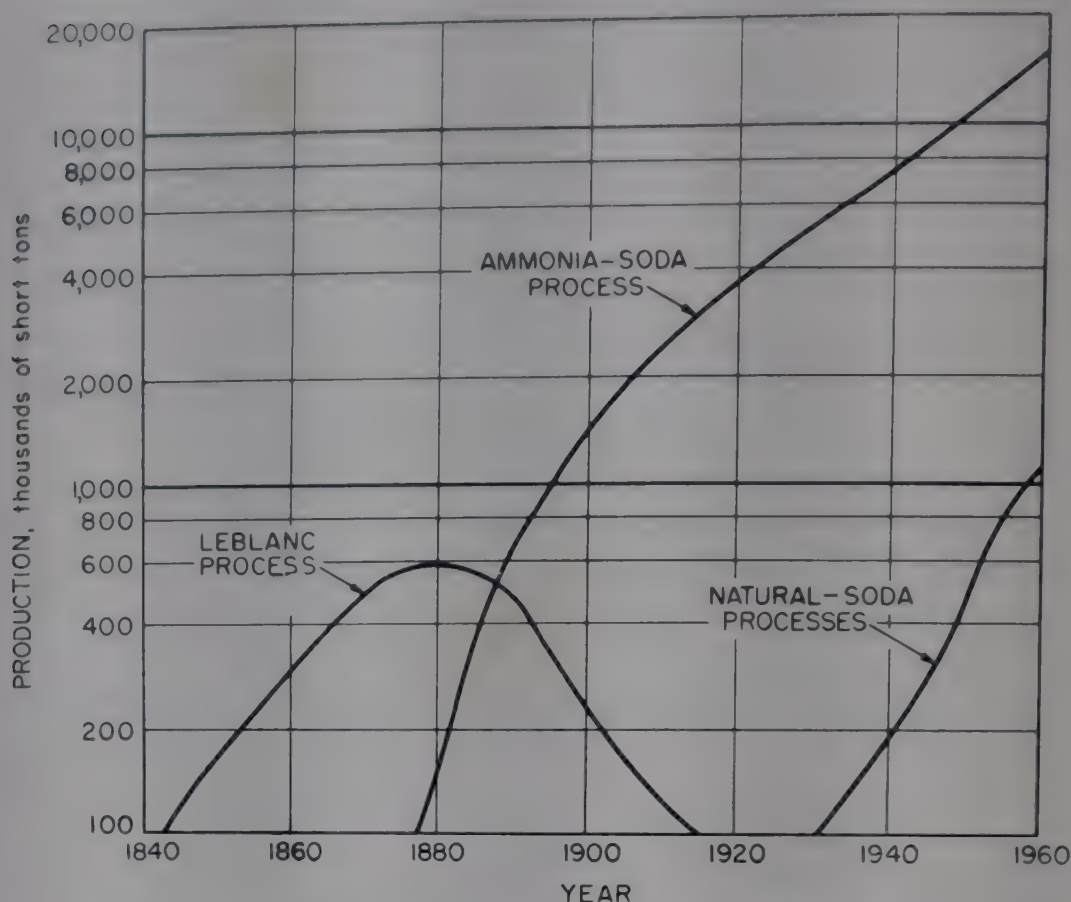


Fig. 3. World production of soda ash in short tons per year.

INDUSTRIAL HISTORY

Natural Soda. Man's earliest use of alkali was undoubtedly prehistoric. Mineral deposits of soda ash exist in a few places in the world. The sands and clays of certain places in deserts often show substantial concentrations of sodium carbonate and in a few rarer cases, quite substantial deposits of reasonably pure sodium sesquicarbonate are found in a form which geologists now term "evaporites." Such deposits have been observed in actual formation during the last 100 years in several of the salt lakes of California and in the large African lakes on the Tanganyika-Kenya border. Probably the earliest examples of Egyptian glass were made of alkali leached out of surface clays at Wadi Natron (an upper Nile tributary), and it is said that Wadi Natron gave sodium its latin name. The ashes of many plants are known to have been leached for alkali in the Middle Ages. Notably the seaweed or kelp of the Spanish coast was the principal source of alkali for Europe during the closing years of the eighteenth century. During recent decades new "natural" productions, based on United States, Kenya, and Mexican brines or minerals, have become more prominent (see p. 738).

Leblanc Process. The earliest process for soda manufacture from salt, outside the laboratory, was the Leblanc process, which enjoyed its greatest prosperity from about 1875 to 1885 (see Fig. 3). This process was entirely displaced shortly after World War I, and it is mentioned here only because of its historical interest. Through it, the chemical industry developed some of its most valuable methods. Nicholas Leblanc outlined his process for the manufacture of soda ash and other chemicals from common salt through the incentive of a substantial monetary award offered by the French Academy of Sciences in 1775. The offer of such an award is indicative not only of a shortage of natural soda, which must have been felt with increasing intensity during the late eighteenth century, but also of the changing civilization of the period

Table 1. Typical U.S.A. Soda Ash Analyses^a

Constituent	Usual specification limits, %	Light ash, %	Inter- mediate ash, %	Dense ash, %
Na ₂ O	58.0 min	58.2	58.2	58.2
Na ₂ CO ₃		99.5	99.5	99.5
NaCl	0.40 max	0.20	0.25	0.25
Na ₂ SO ₄		0.015	0.015	0.015
SiO ₂		0.003	0.003	0.003
Fe ₂ O ₃	0.003 max	0.002	0.002	0.002
CaO		0.016	0.016	0.016
MgO		0.003	0.003	0.003
H ₂ O	0.50 max	0.20	0.20	0.20
water insoluble	0.04 max	0.02	0.02	0.02

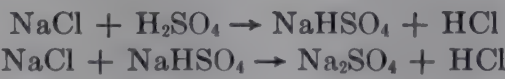
Granulometry: U.S.A. sieve standards

retained on 80 mesh	9.0		
through 80, retained on 100	6.0		
through 100, retained on 120	8.0		
through 120, retained on 140	10.0		
through 140, retained on 170	20.0		
through 170, retained on 200	11.0		
through 200	36.0		
retained on 20 mesh		trace	0.5
through 20, retained on 30		1.6	16.0
through 30, retained on 40		14.3	22.5
through 40, retained on 50		18.5	22.5
through 50, retained on 70		24.4	19.5
through 70, retained on 100		21.9	13.5
through 100, retained on 140		10.5	4.0
through 140, retained on 200		5.2	1.0
through 200		3.6	0.5

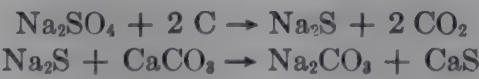
^a European ash is similar except NaCl ranges from 0.3 to 0.6%. African natural soda is high in NaF—up to 1.5%. British “granular ash,” based on a single published reference (2), seems to be, on the whole, finer although both lumpier and dustier—that is, less well-screened.

just before the French Revolution. The revolution itself interfered with Leblanc’s development of his process and his death occurred before he saw the fruits of his genius. The first factory to produce by Leblanc’s process was built in England in 1823 and from then until 1885, the Leblanc process led in the production of soda ash. The industry adopted standardization and its own nomenclature (3).

In the Leblanc process, common salt was treated with sulfuric acid to make sodium sulfate and hydrochloric acid:



The sodium sulfate was heated with limestone and coal to produce “black ash,” which contains sodium carbonate, calcium sulfide, and some unreacted coal.



The sodium carbonate could be water-extracted from the black ash and causticized with quicklime; methods were developed for recovering the sulfur from the calcium

sulfide. The hydrochloric acid was worked up into bleaching powder by the Weldon or Deacon process (see p. 674).

In most of the Leblanc plants the manufacture of sulfuric acid was included, often from iron pyrites and Chile saltpeter by the chamber process. In the largest Leblanc plants, pig iron and metallic copper from the burnt pyrites were additional products. Thus the manufacture of most heavy chemicals had its start in the Leblanc industries.

The Leblanc process was still being practiced in England and on the European continent during World War I, but had entirely disappeared before World War II. It did not make pure products except by expensive recrystallization, which was often done by the customer at his own glass or soap factory; a tremendous amount of burdensome and oppressive labor was involved in the many batch operations; the line of products was exceedingly complex and the market for each product seldom stayed in balance with the quantity produced; and noxious gases and malodorous wastes had to be disposed of. For all these reasons it could not compete with the simplicity and greater economy (in spite of low salt efficiency) of the ammonia-soda process.

Solvay Process. The discovery of the chemistry involved in the ammonia-soda process can be traced back as far as the early 1800's. An unsuccessful factory was actually built in England in 1840. Enough patents, covering various parts of the process, were issued in England and in France to show that all of the basic ideas had been discovered and patented before 1850. A few British and French plants were put into operation in the years 1840-1860, but all of them failed to be commercially successful, owing in part to the difficulties of control that are inherent in the process, and in part to high salt costs resulting from salt taxes then in force.

In 1861 Ernest Solvay independently rediscovered the whole process, and in 1865 he started the first really successful plant, still in operation, at Couillet near Charleroi in Belgium. The plant had a production of 1.5 tons per day in 1866 and by 1872 had reached 10 tons per day. In that year the largest of today's European plants was being built in Dombasle, near Nancy, in France. In 1874 the first successful ammonia-soda plant was erected in England, and in 1882 the first American plant, which is today among the largest in the world, was erected at Syracuse, New York.

There are in the world approximately seventy factories practicing the ammonia-soda process. The maps of the United States and the world, Figures 4 and 5, illustrate the approximate national capacity and geographic distribution. From these it is apparent that alkali manufacture is a good yardstick of "industrialization." For example, Brazil in 1960 completed its first small soda ash factory suitable to the demands of a population in excess of 60 million, whereas Switzerland's single factory, built in 1915, had a 1960 capacity of the same order as Brazil to supply the demands of a population of less than 5 million. The first factory in India achieved regular operation during World War II, and by 1960 India and Pakistan together manufactured approximately 60% of their soda ash consumption in five or six factories for a population exceeding 400 million.

Description of the Solvay Process

Chemical Reactions. The following description is not intended to illustrate the chemical mechanism of the reactions, but to show, as far as possible, how the substances used in the process react in the pieces of equipment which the industry has developed

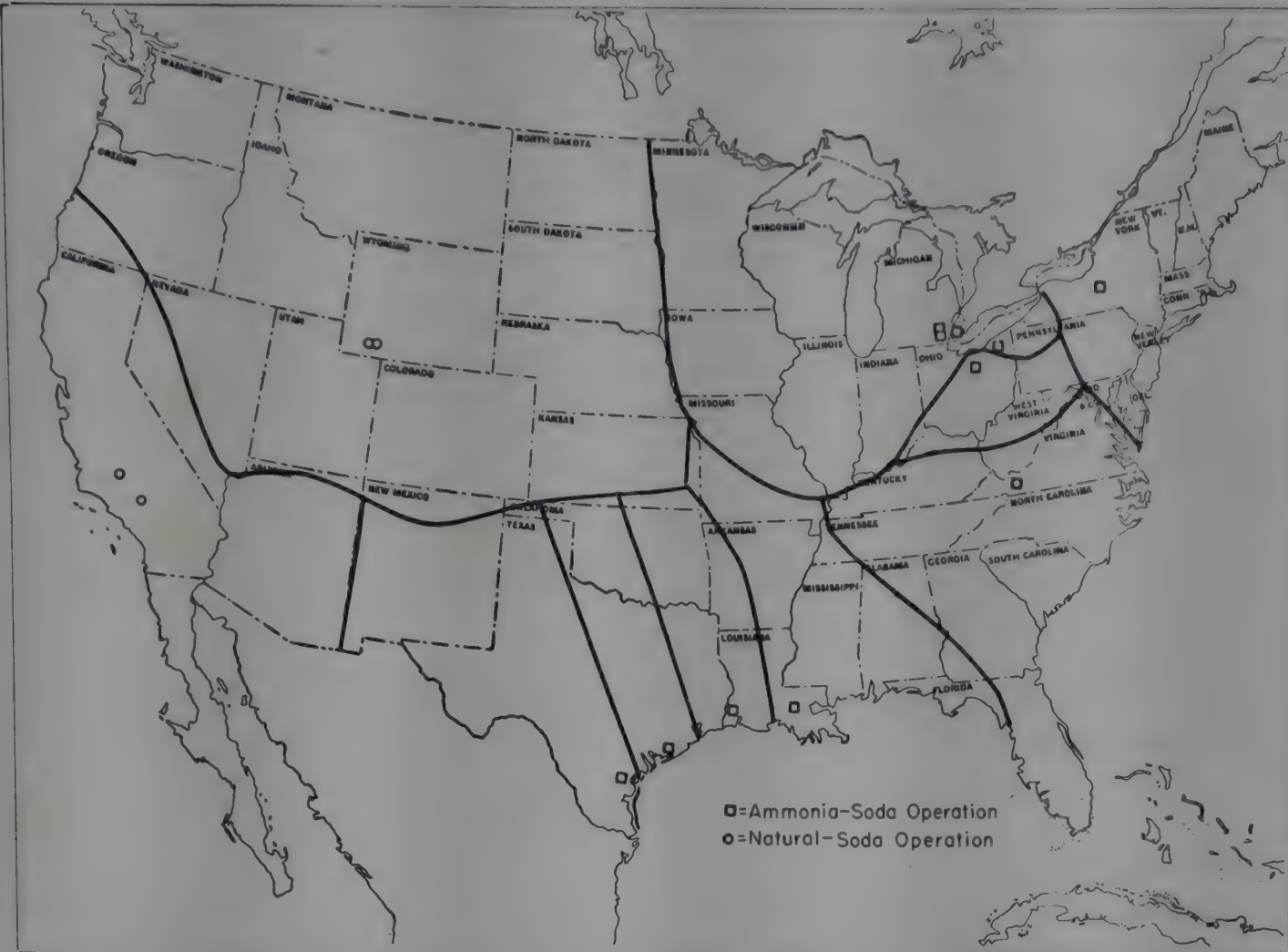


Fig. 4. Soda ash plants in the United States. Heavy lines represent estimated freight boundaries between the plants.



Fig. 5. Estimated daily capacity of soda ash by countries. Area of the symbol is proportional to total estimated daily capacity for country.

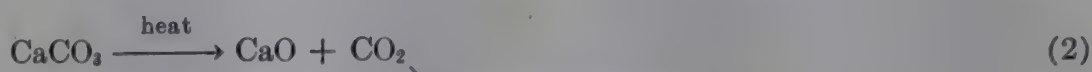
over the years. For this reason the equations have not been written in the ionic form.

The raw materials are common salt and limestone. Ammonia enters into the process, but is not used up and only a very small amount is lost; consequently, it is not a raw material in the usual sense of the term.

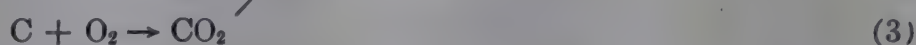
The overall equation for the entire process can be written



This reaction cannot take place directly, but is achieved in a number of steps. The process is cyclic, and in any description it is necessary to begin at an arbitrary point and to return to it. It is convenient to consider as the first step the burning of limestone with coke in a kiln.



(to reaction 5)

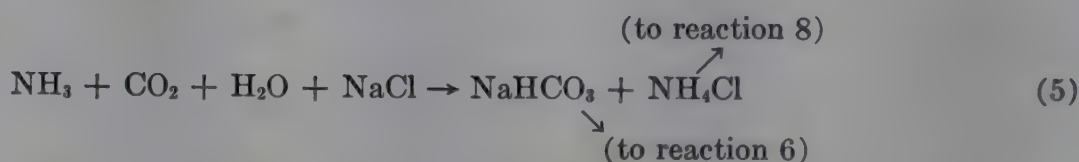


The lime is discharged from the kiln and slaked with water to form a thick milk of lime (see description of the "dry lime" process given on p. 723 for the exception).



(to reaction 8)

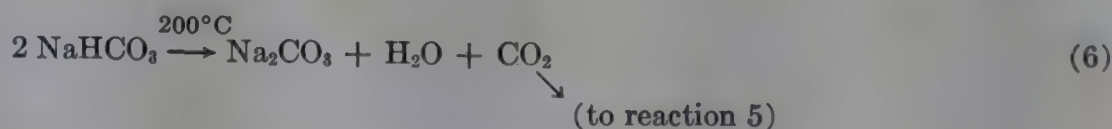
Common salt, in the form of a saturated brine, is treated with ammonia and with carbon dioxide to precipitate sodium bicarbonate inasmuch as it is insoluble in the presence of ammonium chloride. The reaction that takes place can be represented as follows:



(to reaction 8)

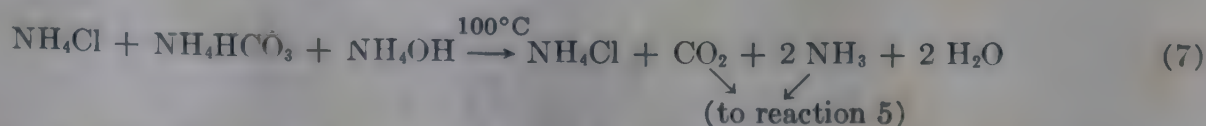
(to reaction 6)

The filtered sodium bicarbonate is decomposed, yielding the carbonate, by heating at a temperature of about 200°C.



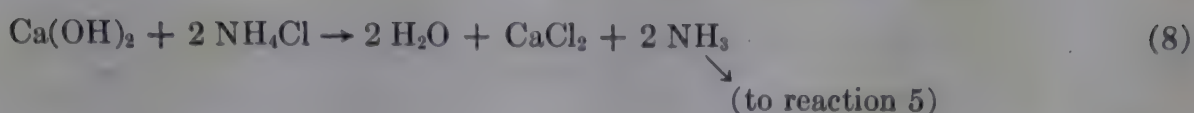
(to reaction 5)

The filtrate from reaction 5 contains ammonium chloride, some unchanged sodium chloride, and the excesses of both ammonia and carbon dioxide; the latter probably exists as bicarbonate ions, although the ammonia is not fully bicarbonated. All of the ammonia must be recovered from this solution. This is done in two steps because heating alone suffices to drive off the ammonia corresponding to the bicarbonate and hydroxide ions, but lime is required to recover ammonia from the ammonium chloride. The first step can be represented as follows:



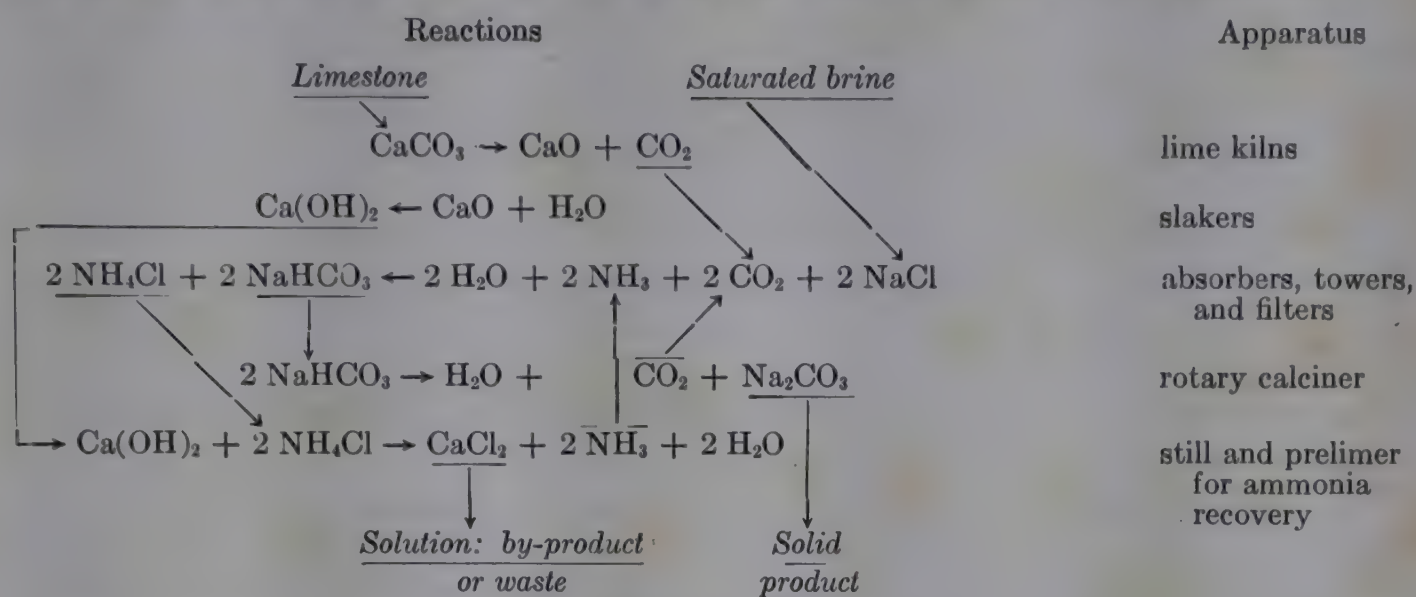
(to reaction 5)

The hot solution, containing only ammonium chloride (and unreacted salt not shown in the above equation), is then treated with the milk of lime from reaction 4.

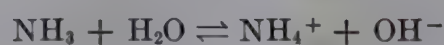


This is known as the "prelimer" reaction.

These equations are now assembled and arranged, with two of them written with the unusual left arrow to facilitate following the flow of materials. The number of moles is chosen to balance the overall equation 1. (Reaction 3, the burning of the coke in the lime kiln, is omitted here, as is the recovery of the "free" ammonia.)



The Role of the Ammonia. Equation 5 represents only the overall reaction. A better idea of the mechanism of the reaction can be obtained by considering the ions that are probably present in the solution. The brine contains the ions Na^+ and Cl^- . When the ammonia is added, it reacts to some extent with the water, giving an alkaline solution.



When the carbon dioxide is added to this alkaline solution, it gives appreciable concentrations of HCO_3^- .



Therefore, in the final solution the ions present in appreciable concentration include Na^+ , NH_4^+ , Cl^- , HCO_3^- , and OH^- . The solubility relationships of the various combinations of these cations and anions, at the concentrations that are met in commercial practice, have been explored by investigators working mostly to provide private data for some of the larger alkali manufacturers. Some early published data are presented in the work of Fedotiev and Koltunov (4) and quite a pyramid of new presentations has been built up from this meager base. One of the reasons that equilibrium solubility relationships have not been exhaustively studied nor prepared for publication is in part due to the fact that to the equipment designer, reaction rates are of considerably greater importance than equilibria. The process is not only cyclic, but each of the steps has, almost from the beginning, been carried out on a continuous basis, with the optimum approach to equilibrium determined empirically on a plant (or equipment unit) basis.

Sodium bicarbonate is the only reasonably common sodium salt having a low solubility compared to most sodium salts, and its significantly low solubility under the conditions prevailing in the Solvay carbonating tower is the fundamental fact under-

lying the success of the Solvay process. It enables nearly complete and clean separation by the simple operation of filtration, thus permitting adequate recovery of the ammonia.

Equation 5 gives no indication as to the order in which the reactants should be brought together. If ammonium bicarbonate is prepared and brine is added, the process is unsuccessful. It can be made to work with ammonium bicarbonate and solid salt, but this is inconvenient from an engineering point of view, and the product does not have a good crystal form. When brine is used, it is essential to absorb the ammonia in the brine first, before any large quantity of carbon dioxide is added. This discovery, and the recognition of the need for continuity in the process, are the two outstanding contributions that finally gave Solvay success where many others had failed.

Equations 1 through 8 above have been written with a single-headed arrow to indicate the direction in which the reaction proceeds in the course of the process. Actually, they are all reversible reactions, and for scientific accuracy should be written with double-headed arrows. In reaction 5 complete bicarbonation of the sodium salt is never obtained, and the reaction is carried only as far as has been found to be profitable.

In ammoniation, the solubility of ammonia in brine depends on the concentration of the brine, the presence of carbon dioxide in the ammonia, and the temperature. Reasonably economical operation is possible only if the brine entering the absorber is saturated, or nearly so. The ammonia concentration is limited by practical considerations—sodium bicarbonate crystals in a size and form suitable for filtration, and the most efficient use of the heat-interchanger surfaces in the ammonia-still condenser and in the ammoniacal brine coolers. Ammonia absorption is usually carried to about 85 grams ammonia per liter. The solution of ammonia in brine is exothermic, and the above concentration cannot be reached without cooling the liquor. The ammonia gas obtained from the ammonia still contains sufficient water vapor so that when it is dissolved in the nearly saturated brine, no sodium chloride is precipitated, although the solution continues to be nearly saturated with sodium chloride. The latter is a necessary condition for a satisfactory yield of bicarbonate. Occasionally, with a brine unusually close to saturation and with an exceptionally efficient ammonia still, sodium chloride crystallizes out on the cooling surfaces of the ammonia absorbers.

The carbonation of the ammoniacal brine is a complex process, both theoretically and in practice. Particularly in the "making tower" the following factors are involved: several mechanisms of transport of ionic reactants through and across gas-liquid interfaces; the nucleation of a crystal phase; the growth of solid crystals kept in suspension through gas agitation; and the several aspects of removal of heat of reaction. High rate of reaction is favored by high (relative) temperature, high concentration of CO_2 throughout the tower, and intimate mixing. High conversion of chloride to bicarbonate (salt economy) is favored by high CO_2 gas pressure and concentration and the optimum cooling control at the slurry exit. Too low an exit temperature gives mixed ammonium and sodium bicarbonate crystals. Economy of CO_2 gas utilization is favored by a low CO_2 concentration in the vent gas (favoring tall towers), whereas economy in gas compressor power utilization favors squat towers. Close approach to equilibrium favors slow throughput, whereas best utilization of investment favors fast throughput. The industry has evolved a fairly uniform practice which achieves a salt conversion of 72-76% when controlling the temperature of the

bicarbonate slurry to about 28°C. The carbonators so used are 80–90 ft high with 73–77% CO₂ entering the bottom, 37–42% CO₂ entering the middle, and 5–7% CO₂ vented from the top.

For favorable yields, more than the theoretical equivalent of ammonia (as indicated by eq 5) must be present, and, in practice, about half a pound of ammonia is recycled per pound of sodium carbonate made. Ammonia is worth at least three times as much as soda ash, so for profitable operations the ammonia losses must be kept extremely small. The best of today's factories lose less than 2 lb of ammonia per ton of soda ash sold. Such a high recovery for so volatile a material is the result of years of struggle to develop both equipment and practices.

Figure 6 is a flow sheet showing diagrammatically the essential pieces of engineering equipment in a modern ammonia-soda factory. The intermediate liquors pass through a number of storage vessels which, although essential to successful operations, are omitted from the flow diagram for simplification. The storages have a chemical as well as a physical significance, which will be referred to in greater detail under "Operation and control," p. 723.

Ammonia Absorption. The strong brine from the wells, after purification (see p. 725), is saturated with ammonia gas in a tall cast-iron absorption tower. Here also a corrosion inhibitor, usually a sulfide, is added to protect the quality of finished soda. The ammonia gas contains some water vapor and carbon dioxide, but this will be referred to in greater detail on returning to this point of the cycle. During ammoniation the brine requires extensive cooling to permit the necessary high degree of saturation at close to atmospheric pressure (approximately 390,000 kcal per metric ton of soda ash sold). The brine enters this process as cool as practicable, at about room temperature or slightly lower, and it is first used to scrub the residual ammonia from the exhaust gases, which are returned from other points in the cycle. The operation is generally carried out at slightly less than atmospheric pressure. The brine descends through the main part of the absorber countercurrent to the rising ammoniacal gases. When raw brine (containing the usual calcium and magnesium impurities) was used, the absorber reaction precipitated these as calcium carbonate and magnesium hydroxide; such ammoniated brine was then passed through settling vats. The sludges were pumped out of the settler bottoms and added to the liquors from which ammonia was distilled. In most modern plants, however, the brine is prepurified by precipitating the calcium as carbonate and the magnesium as hydroxide, usually with soda and lime. The resulting sludge from such an operation is ammonia-free and thus needs no treatment prior to disposal, but the biggest advantage of prepurification is reduced absorber cleaning and the resultant interruption-free, long-term absorber operation. Much lower insolubles content in the soda ash is another big advantage of prepurification.

Precipitation of Bicarbonate. From the settling vats (or directly from the absorber coolers with prepurified brine), the clear ammoniated brine passes through storage reservoirs and is then pumped into the top of a high "Solvay" tower. Into the bottom of this tower, lime kiln gas, compressed to about 45 psi, enters and bubbles up through the solution so that most of the carbon dioxide is absorbed. The nitrogen, which is about 60% of the lime kiln gas, is vented from the top of the tower into a general vent system. This step of the precipitation process is called the "cleaning," and is controlled (CO₂ not to exceed 66–73 grams per liter) so as to be well below the carbon dioxide concentration which forms a precipitate. Relatively little cooling

(35,000 kcal per ton) is required. The function of this tower will be described after the next step. The liquid flowing from the bottom of the cleaning tower is pumped to the top of a "making" tower (actually several towers in parallel) where the same process takes place with stronger carbon dioxide gas, partly from the bicarbonate calciners, bubbled up through the solution. The process precipitates sodium bicarbonate and is accompanied by the evolution of considerable heat (410,000 kcal per ton) so that the apparatus must be cooled extensively in order to improve yield, and the cooling must be controlled to form good crystals. Some of these crystals, and also crystals of other solid phases, form on the cooling surfaces (and all other surfaces as well), producing a typical scale which soon reduces the effectiveness of the cooling surfaces. The towers thus require "changing;" by this is meant that a "making" tower becomes the "cleaning," or precarbonating tower. The scale is dissolved off the cooling surfaces during cleaning by the fresh ammoniated brine, assisted by the agitation of the cleaning gas, which at the same time precarbonates the brine to the point at which precipitation is imminent.

The nitrogen gas (containing 3–7% carbon dioxide and some ammonia), vented from both the cleaning and making towers, is collected in vent mains and conducted to an apparatus that is really a part of the absorber mentioned in the previous section, where the freshest brines scrub out substantially all the residual ammonia. The vent gases are at slightly greater than atmospheric pressure at the top of the carbonation towers, and when released to the atmosphere from the tower-vent gas washer, carry off about 5% of the total ammonia loss (that is, approximately 0.01 lb NH_3 per ton).

Filtration of Bicarbonate. The slurry "draws" from the several making towers being operated in parallel are collected in a single small vessel in order to minimize the effect of the imperfect crystals that are generally obtained during the early hours of operation of the "new tower" after its change. From the small collecting vessel, the slurry is fed to continuous filters. The rotary vacuum filter was invented for this process and still leads all other equipment used for the purpose, but improvements in continuously operating centrifuges have induced several manufacturers, particularly in Europe, to try such equipment again even though in some of the oldest plants it had been replaced by vacuum filters. The filter cake is washed with a carefully controlled amount of fresh water at slightly above room temperature in order to control the residual chloride to that demanded by the customers of the factory. The average European soda ash is higher in salt content than the American product (about 0.5% NaCl for European soda and 0.2% for American soda). The filter or centrifuge wash is essentially a displacement of the mother liquor. A cake which contains from 9 to 18% moisture is continuously delivered. The filter vacuum air (or the vent gas from the centrifuge operation) is scrubbed with fresh brine as part of the absorption process or by the entire fresh brine stream on its way to the absorbers. The filter cake, often called "crude bicarbonate" or "ammonia soda," contains, besides the diluted mother liquor and the sodium bicarbonate, an average of approximately 5 mole percent of ammonia. Part of this (particularly at too low a draw temperature) is crystals of ammonium bicarbonate, but a very substantial part is as solid solution of NH_3 in NaHCO_3 . The ammonia content hardly goes down when the wash-water volume is substantially increased, whereas the resulting sodium chloride concentration is greatly reduced. The ammonia in the brine being carbonated influences the crystal habit of sodium bicarbonate, so that under a microscope the crystals have a unique form quite different from that of a pure bicarbonate solution. The crystals are highly vari-

able, tend toward complex twinning (called daisies) under certain conditions, and always tend to change to a mushy form, making filtration very difficult if the carbonator conditions are in any way "wrong." Freshly filtered bicarbonate gives no coloration to phenolphthalein, but the color gradually appears and becomes quite strong before the damp bicarbonate reaches the calciner feed. The loss of carbon dioxide which is entailed in this change carries with it one of the biggest parts of the ammonia loss.

After its removal from the filters, the cake is conveyed continuously to the calcining operation. A storage pile to provide the "come and go" between the carbonation and calcination steps is needed. The crude bicarbonate is here handled in the solid state (not as a pumpable slurry), and it is undergoing changes (losing CO_2 , becoming alkaline) during its handling which tend to cause exceptional difficulties of arching, caking, and clinging to the sides of bins. Much manual labor used to be involved in adding to or reclaiming from such a stockpile. In modern factories, stocking and reclaiming is largely avoided (in order to minimize gas imbalance irregularities) even though plastic bin- and chute-lining materials have been found (5) that greatly facilitate conveying.

Calcining the Bicarbonate to Soda Ash. The crude bicarbonate from the filters is continuously calcined in cylindrical rotary equipment. The earliest calciners were scraper-equipped, externally fired, shallow "Thelen pans," but these were long ago replaced by level cylindrical shells externally fired with coal, oil, or gas. During the mid-twentieth century, these rotary externally fired calciners were being replaced with steam-heated rotary shells, packed with finned tubes designed for 450 psi steam. Fluidized bed techniques have been patented (6) but not yet put into use in the United States. But all of them function to heat the product (580,000 kcal per ton) to a final temperature ranging from 175 to 225°C in such a way that all of the gas generated by the decomposition of the sodium and ammonium bicarbonates can be led away, with minimum dilution, giving a gas at 95% CO_2 or higher. The gas is extensively cooled to remove as much of the water vapor as practicable (225,000 kcal per ton) and is then mixed with the makeup kiln gas for delivery to the bottom-entry carbonation operation.

Storing and Shipping of Product. The hot soda ash from the discharge end of the calciner is cooled and then stored either in rooms or cylindrical silos designed for large-scale mechanical handling of the material. From the silos or storages the product is screened and packed for shipment in paper or burlap bags and barrels. Much of it is shipped in bulk. A large part is conveyed to other operations in the same factory for producing dense soda ash, refined bicarbonate (see Sodium compounds), caustic soda (see Sodium hydroxide, p. 740), and glass (qv).

Dense Ash. A coarse-grained soda ash, called dense, heavy, or granular, is used in glass manufacture because it is dustfree and mixes better with sand and lime. Chemical analysis of the dense product is substantially identical to the light product (see Table 1).

The most widely used method for making dense soda ash involves recrystallizing as sodium carbonate monohydrate (with a precisely controlled excess of water) and then again heating to dehydrate the enlarged crystals. Monohydration is accomplished in mixers or blenders in which feed rates of water and light ash, as well as temperatures and holding times, must be nicely controlled to assure the preferred graining. The product from the mixer (or monohydrator as it is often called) is delivered directly to a continuously operating dryer. Several types are in use: an externally fired

cylinder similar to the calciner; internally fired cylinders where gas or oil fuel fires are operated countercurrent to the flow of soda; steam-heated dryers similar to the light-ash calciner mentioned above; rotary hot-air-swept dryers; and fluidized bed techniques wherein the products of combustion and drying are the fluidization medium. The dehydrated product from any of these dryers needs only screening to remove oversized lumps and undersized dusts before packing and shipping. Most dense ash is shipped in bulk because it is used almost entirely by large industries. Recently a minor amount of dense soda has been reaching both American and West European markets, made by briquetting anhydrous light ash under high pressure and then crushing and screening. The briquettes themselves and the coarse grindings find application in iron foundries.

Recovery of Ammonia. The mother liquor, filtrate, or "filter liquor" from the continuous filters contains substantially all of the ammonia with which the brine was originally saturated. The rest is in absorber "muds," calciner gas condensates, etc. A part of that in the filtrate is present as "free" ammonia—that is, ammonium hydroxide, bicarbonate, and carbamate, and the several possible carbon compounds of ammonia that decompose at moderate temperatures; the remainder is present as "fixed" ammonia or ammonium chloride, stoichiometrically corresponding to the sodium bicarbonate that has been precipitated. The filter liquor also contains the unreacted common salt. In the larger plants, the muds removed from the ammoniated brine settling vats, and the diluted ammonia solution resulting from cooling of the gases coming from the calciners, are distilled in separate columns, since no lime reaction is required, and steam which is flashed off from the regular distiller blowoff can be used for the purpose.

The ammonia still is the most expensive single piece of equipment in the plant, and the one that requires the most accurate control. It is usually a very tall tower whose uppermost portion contains water-cooled tubes to condense some of the water vapor out of the ammonia gas generated in the lower portions. Just below the condenser is a preheater, where the feed-liquor is preheated, and in so doing, more water vapor is removed from the gas by condensation. The warmed feed-liquor then enters the main coke, tile, or bubblecap-filled section, where heat decomposes the free ammonium compounds and steam sweeps the free ammonia and carbon dioxide almost entirely out of the liquor.

The Lime Reaction. The carbon-dioxide-free solution is treated with milk of lime in an external liming tank called a preliimer. Most of the evolved ammonia gas is vented from the preliimer back to the rectifying column. The preliimer requires quite violent agitation since the heavy particles of undigested lime react rather slowly. The resulting hot calcium chloride solution, containing the residual ammonia in the form of ammonium hydroxide, is led back to the top of a 10–14 plate still. Exhaust steam from gas compressors and other mechanical operations of the plant is blown into the bottom of the still and sweeps practically all of the ammonia out of the limed solution. The solution, which is known as the still waste or still blowoff, contains calcium chloride, unreacted sodium chloride, and the excess lime, and is diluted by the water in which the lime was conveyed to the reaction and by the condensed steam, and is contaminated with all the sulfate and lime impurities. In a few plants a part of this solution is worked for the recovery of calcium chloride (see Calcium chloride under Calcium compounds) but most of it is pumped to waste. Large impounding reservoirs are used to settle solids from this waste before it can be released to the adjacent water courses.

In the earliest Solvay plants, the lime was added intermittently as lumps of CaO , directly from the kiln bottom, in a steel basket lowered into the preliher. The advantages of lower dilution and recovered heat of reaction, which are obtained with dry lime, were later sacrificed to gain the low labor and precise control of continuous feed of milk of lime. In the new (1958) efficient plant of Koninklijke Nederlandse Soda-Industrie, anhydrous lime is again being used, but it is fed continuously as finely pulverized material. This reduces fuel consumption quite markedly.

The control of the distillation operation is difficult and involved because the carbon dioxide must first be thoroughly stripped in order to avoid waste of lime, and thereafter the ammonia must be driven off entirely in order to bring the loss of this expensive chemical to a tolerable level. On the average, 10% (0.2 to 0.6 lb ammonia per ton) or more of the ammonia loss is in the still blowoff.

Actually, ammonia leaves the top of the lime still as vapor in equilibrium with water; these gases furnish the heat used in the heater ("free NH_3 " still) section where "free" ammonia is decomposed. The preheater and condenser cool the resultant gases, the ammoniacal condensates acting as reflux, concentrating them with respect to ammonia and carbon dioxide. All of the gas at about 56°C (solid carbamate crystals sublime at a lower temperature) is led to the brine absorption tower referred to at the beginning of this description. There, most of the carbon dioxide is absorbed along with the ammonia; the remainder is part of the noncondensables which are scrubbed with the freshest brines and then removed by the absorber vacuum pump to be added to the calciner and kiln gas mixture used for carbonator bottom-entry gas.

Lime Preparation. (See also Lime and limestone.) The most suitable limestone is hard and strong with low concentrations of impurities (silica is the least desirable) and is graded to reasonably uniform coarse size (4 to 8 in.). Most soda ash manufacturers, especially in the U.S.A., operate private quarries and consequently keep the quality control of selective mining in their own hands. When purchasing limestone for soda operations, the specifications are fairly rigid. In modern burning practice the screened limestone is elevated to high bins from which it is mixed with metallurgical-grade coke to about 7% of the stone weight. This mixture is then fed periodically into the tops of tall kilns (60 to 100 ft of shaft). Air is blown continuously into the bottom of the kiln, gas is sucked off the top, and the coke burns in a zone a little below the middle of the kiln. The charge there reaches about 950 to 1100°C , at which temperature the stone "burns" to lime. The carbon dioxide evolved consists of both that generated by the decomposing limestone and that resulting from combustion of the carbon in the coke. The kiln gases are considerably diluted with nitrogen from the air used to burn the coke; they usually contain from 37 to 42% CO_2 , together with stone dust, coke ash particles, and gaseous impurities. The gas is cooled to some extent in the kiln itself by the upper layers of stone; it is further cooled and purified in water scrubbers until it is almost free from dust and tarry matter, and then, in the more modern plants which make a very pure soda ash, the gas is finally purified electrostatically. The pure gas is conducted to the inlets of compressors that pump into carbonating towers. For oyster shells and other forms of more finely divided calcium carbonate, such as fines from stone-screening operations, or the softer oölitic stones, rotary kilns are in use. Owing to their relatively large radiating surface and comparatively poor contact between gas and solid, rotary kilns have a lower fuel efficiency than the vertical kilns, making the concentration of carbon dioxide gas significantly lower. Furthermore, the difficulty in maintaining an adequate flame

with the combustion of fuels of low volatility, such as pulverized coke, or even petroleum coke or mixtures of these, requires a considerable fraction of hydrogen in the fuel and this, of course, further lowers the carbon dioxide concentration in the resulting kiln gas. Some of these kilns are operated with natural gas, giving a carbon dioxide concentration of 25–28%. With certain alterations in equipment, satisfactory soda can be produced with such gas, often with an overall gain in economy owing to the cheapness, ease of handling, and perfect control possible with natural gas.

The lime, cooled somewhat by the entering air in the lower parts of the shaft kiln (or in appropriate coolers beyond the discharge point of the rotary kiln), is discharged periodically, passed through storage bins, and is then continuously slaked to calcium hydroxide with an excess of water, usually in rotary slakers that produce a thick suspension, commonly called milk of lime, *lait de chaux*, *Kalkmilch*, etc. The heat of the reaction is such that the milk is discharged at a temperature of 90 to 100°C, and the water flow is controlled to give a free calcium oxide content of 230 to 300 grams per liter. The milk is stored in tanks provided with powerful agitators. In the dry lime operation, of course, the lime is stored in bunkers both at the lime plant and also near the distillation operation where it is convenient to operate the pulverizing machinery.

Source of Power. The various pumping and compressing operations described in the foregoing paragraphs require considerable power, so that all ammonia-soda operations have a central power plant where steam and electric power are generated. Electric motors are almost invariably used for the many “mill drives,” such as conveyors, tank agitators, centrifugal pumps, packing machinery, etc, whereas in the older plants the larger drives—for example, those for cooling water pumps, gas compressors, and filter vacuum pumps—were often steam engine- or turbine-driven, non-condensing. The exhaust steam from the mechanical drives added to that from the electric generators was used for distillation of the ammonia. In a well-designed and operated plant of this type, the steam cycle was usually “in balance” and the total consumption of fuel for all operations was generally well below 0.4 pound of coal per pound of soda ash sold. Most soda ash plants today have become complicated by a large number of satellite operations, such as chlor-alkali, calcium chloride, chlorinated organics, and even cement and sodium chromate, so that the central power plant has a much bigger job to do than formerly. Furthermore, the recent modernizations, especially those involving calcination with steam-heated equipment, have altered the steam electric power balance so that it is almost invariably necessary either to purchase electric power, or else to operate a substantial part of the electric generating system on a condensing cycle. This has resulted in higher overall thermal efficiencies; thus, in the modern soda ash plant, when the heat and power requirements are recalculated on the old efficiency basis, the coal consumption is seldom as high as one-fourth pound of coal equivalent per pound of soda ash produced.

Operation and Control. The ammonia-soda plant, as a whole, is operated to keep the saleable soda ash storage silos about one-half to two-thirds full. In case the shipments decline to such an extent that production rate must be cut back, the first control is to slow down the gas compressors. This sucks less air through the lime kilns, thereby slowing them down. Less gas is pumped into the precipitating towers; consequently, less ammoniated brine is fed to them in order to maintain the same degree of carbonation in the “draw.” As the level of ammoniated brine in the storage vessels rises, the rate of feeding filter liquor to the ammonia distiller is reduced, and

the brine flow to the absorber is slowed down to hold the NH_3 titer at target. These are the essentials of rate control.

Since the process is continuous and cyclic, chemical control requires samples of each process liquor to be regularly withdrawn and titrated. Temperatures, pressures, and titers are held as nearly constant as is practicable. Only rates of feed or discharge are varied. The utmost precision and good judgment are required in the operation and control because such large volumes of high-priced constituents are being handled.

The problems involved in a continuous cyclic operation are not fully appreciated by those who have dealt only with batch operations. A most essential requirement of continuous operation is the provision of appropriate storages for intermediate liquors and materials. Such storages must not only be of sufficient size to allow for the "come and go" of the process, but must provide for minimizing the effect of variations in concentrations that are beyond practical control. Storage vessels must therefore not only be of sufficient size but must be of the proper shape and have connections to inhibit lamination, thickening, or short-circuiting. The levels of storage vessels cannot be allowed to rise or fall rapidly even when there is no immediate threat of overflow or running dry. Whenever one operation must slow down in relation to the others, there is bound to be a concentration change which will have an unfavorable effect and require compensatory reregulation all over the process. It is therefore good practice to specify rather narrow tolerances in all aspects of control; only the most skillful organization succeeds in maintaining all of these at their optimum when compensating for the numerous raw materials, climate, fouling, and shipping fluctuations.

The process is well suited to, and has adopted, automation insofar as temperatures, pressures, flow rates, and levels are concerned. Continuous automatic chemical analysis (or titration) is used only in a small number of cases because of the difficulty brought about by the varying amounts of insolubles suspended in most of the liquors.

Description of Apparatus

In sharp contrast to the situation existing in the chlorine industry, no standardized equipment or apparatus is offered by fabricators for use in the manufacture of sodium carbonate. Whereas several manufacturers of cells and patent holders of cell designs offer to design, purchase, and even construct complete liquid-chlorine plants, there is no comparable service available to the soda ash industry. This is partly due, no doubt, to the fact that there are so many more chlor-alkali plants than there are soda ash plants, and this is true in every country which has a soda ash plant. Brief descriptions and outside dimensions of the principal manufacturing equipment developed and in use by the industry during the early 1960's are given below.

Lime Kilns. (See also Lime and limestone.) A modern lime kiln with a capacity of 200 to 500 tons of stone per day is approximately 12 to 16 ft in diameter and from 70 to 100 ft high. It is lined with a thick layer of fire brick with an insulating material between the fire brick and an outer steel shell. The top of the kiln is usually sealed to prevent the somewhat noxious gases from polluting the charging deck. Charging mechanisms consist of anything from very simple holes with double conical bells to rather complicated distributing devices for kilns of larger diameter. The discharge mechanism usually consists of devices that will draw the lime out uniformly

over the entire cross section slowly enough to let it cool adequately in the incoming combustion air. Rotary kilns are in use for the burning of oyster shells and quarry fines, and for reburning calcium carbonate sludges from causticizing operations. As such installations are comparatively rare, no standards of size can be stated.

Slakers. The lump lime from the kiln is usually fed directly into horizontal rotary continuous slakers by means of table feeders or weighing-type feeders. The horizontal rotary slaker, which is the most commonly used, is approximately 5 ft in diameter and 60 ft long for a capacity of about 250 tons of soda per day. Both lime and warmed water are fed in at one end and the milk of lime is discharged from the opposite end, which has some mechanism for separating out the undigested particles of unburnt stone or coke. Some of the best slakers discharge at the same end at which they are fed. The lime goes through an inner cylinder, and then returns between the inner and outer cylinders. In the most modern plant where dry lime is fed to the preliher, the entire slaking plant is omitted and a lime crushing and pulverizing system is substituted. As in the case of rotary kilns, there are as yet not enough dry lime plants to have made this type of grinding equipment standard for the industry.

Brine Making (7). In all United States plants and in most of the plants in the world, the brine is prepared directly within the stratum or dome of rock salt that is the supply of the mineral. Where the strata are not sealed from the ground waters, wells are drilled into these waters and, by means of air lifts, brine is removed at the rate appropriate to saturation. Where the stratum is sealed from ground water, water is usually forced down into the cavity at such a rate that a saturated brine emerges from an inner tube within the same well. In those few plants to which solid salt is shipped from mines, the brine is prepared simply by dissolving the salt in highly agitated tanks. Those plants that prepurify the brine before it reaches the absorber treat the material either in continuous or batchwise tanks with controlled streams of soda ash and lime and an underflow which sends the sludges to waste.

Ammonia Absorbers. The usual ammonia absorber is an all cast-iron tower consisting of three or more distinct parts. At the very top, where the freshest cool brine enters, are the scrubbers for the air from the vacuum filters, the carbonating tower vent gases, and final vacuum gases from the main part of the absorber. In modern practice these are tile or coke-packed cast-iron towers with the packing supported on simple grates. The absorber proper is similarly a packed cast-iron tower, but it is arranged with a tray or plate about one-third of the way up, from which brine is removed and cooled in coils to as low a temperature as practical with the local cooling water. These coils are usually cast-iron pipes set in vertical banks, and water is sprayed over them in an outdoor basin. Shell and tube devices of stainless steel and, in some cases, aluminum, had found limited application by 1960. The lowermost part of the absorber, where the greatest part of the ammonia is absorbed, reheats the brine, and it is then cooled or tempered in additional cooling coils. A tower approximately 6 ft in diameter and 80 to 100 ft in total height (for all of its functions) has a capacity of 300 to 500 tons of soda ash per day. The most common practice in the more modern plants and in those being modernized, with respect to the process equipment, is to have but a single set of cooling coils through which a relatively large volume of brine is recycled and from which the "make" of ammoniated brine is shunted off to the carbonation operation. Furthermore, it is now more frequently the case that the entire brine stream is used in a single washer for the filter vacuum air and is then split into several carbonating tower washers and their corresponding absorbers.

Although it has not always been the case, modern plants are arranged for one absorber for each ammonia distiller.

Carbonating Towers. In almost all soda ash plants, carbonation takes place in tall cast-iron towers that are kept substantially flooded with the liquor. The development of these towers was begun by Ernest Solvay; during his lifetime the towers reached sizes of 6 ft in diameter and 80 ft high. The upper parts of the towers contain plates and mushrooms designed to break up the gas stream into a large number of bubbles. These plates are spaced at about 18-in. intervals to combat the bubble-coalescing tendency. The lower half of the tower consists of cooled compartments that contain cast-iron water pipes stretching across the tower, and between each such compartment there is another plate and bubble cap similar to the ones above. A group of five such 6-ft diameter towers has a capacity of about 300 tons of soda ash per day. Most American plants and the more modern European plants now employ carbonating towers 9 to 10 ft in diameter and 80 to 90 ft high. A group of five is normally used; capacities up to a maximum of 1000 tons of soda ash per day per group are achieved.

In a small number of plants operating during the 1960's, carbonation was still being accomplished in what is known as Honigmann apparatus. This consists of five steel vessels, designed for a pressure of about 50 psi, shaped like pears mounted with the small end down. The carbon dioxide gases are pumped into the bottoms of these towers, or rather into the top through a plunge pipe that extends to the bottom, and gas flow through the five vessels is in series, countercurrent to the flow of the ammoniated brine. As the vessel that receives the strongest gas approaches equilibrium, that is, contains the optimum amount of sodium bicarbonate in suspension, it is cut out of the line and changed over to become the first in series of the liquor flow. The Honigmann apparatus is not so standardized as the Solvay tower; however, based on modern plants still using it, a capacity of 500 tons per day requires twenty such vessels about 15 ft at their largest diameter and about 30 ft in total height. Although the Honigmann plant requires a high investment and a considerably larger attendant labor demand, it is said to produce a much more consistently filterable bicarbonate.

Filtration of the Bicarbonate. In the United States this step is carried out on fairly standard, continuous, rotary vacuum filters. In Europe and elsewhere, both rotary vacuum filters and also cycle-controlled, continuously running centrifuges are in use. (See Centrifugal separation; Filtration.) The filters are generally all cast-iron construction, have a larger number of pressure rolls than usual, and operate at a somewhat higher vacuum than is used with most granular materials. A filter 6 ft in diameter with a 6-ft-wide face has a capacity of 100 to 150 tons of equivalent soda ash per day. Most modern plants are now equipped with larger filters, some 9 ft in diameter with a face 7 ft or wider; these operate up to capacities of 500 to 600 tons of soda ash per day. On the other hand, cycle-controlled centrifuges of the order of 8 ft in diameter and operating at 330 to 400 rpm, in a plant with an installation of seven or eight, can maintain a total plant production at around 500 to 700 tons of soda ash per day. Instead of being cycle-controlled, the latest centrifuges offered for this purpose have means for propelling the charge axially, so that it successively passes through zones of purging, washing, and drying, and discharges continuously. Both types of centrifuge give a considerably drier product than does the vacuum filter (8 to 9% moisture as compared to 12 to 18%), but the lower investment seems so far to have favored, by a small and narrowing margin, the vacuum filter.

Calciners. Quite a number of soda ash plants still operate externally fired, cylindrical rotating calciners. The earliest were about 6 ft in diameter and 60 ft long and had a capacity of 50 to 70 tons of soda ash per calciner day. Larger units, 8 and even 10 ft in diameter, have been in use for the past 25 to 30 years; these have capacities of 100 to 140 tons of soda per day. Beginning about 1930, the steam-heated calciner came into use and during the 1960's was rapidly replacing the direct-fired equipment. Most of these steam-heated units are 8 ft in diameter and 80 to 100 ft long and have a capacity of 400 tons per day. Machines with a diameter of 10 ft are also in use but there is hardly any which has a capacity greater than 500 tons per day; the larger diameter is used principally to obtain shorter machines and simpler dedusting of process gas. The fuel consumption of the externally fired machines corresponds to a thermal efficiency of less than 50%, but the steam-heated units have a very high thermal efficiency; for the latter the coal consumption (including steam-boiler losses) per ton of soda is now about three-fourths of what it used to be for this operation alone. Some engineering studies have been made and patents have been issued for calcining crude bicarbonate to soda ash using the fluidized bed techniques developed in the handling of catalysts in the petroleum industry. Patents have also been granted for dewatering the monohydrate for dense ash manufacture by fluid bed techniques. Routine operating data are not available at this writing (1962).

Conveyors and Elevators. The crude sodium bicarbonate can be handled on rubber or metal belts although it is somewhat corrosive to the mechanical parts of these devices. For many years the usual practice was to convey this crude bicarbonate on drag conveyors in steel troughs, since these have the advantage of providing small but useful "live" storage of material. Conveyors for the hot soda ash are usually screw conveyors of somewhat special design, although recently the Redler type of conveyor has come into considerable use. Freshly calcined soda ash is too easily blown away and too hot to be conveyed on rubber belts. Some soda ash is conveyed pneumatically and this is especially appropriate for vertical rather than horizontal movements, but has two disadvantages: (1) the conveying air must be very dry to avoid caking troubles; and (2) the conveyed soda frequently loses a part of its flowability—that is, becomes even less free-flowing.

Ammonia Still. A complete ammonia still (including heat recuperation auxiliaries) for 250 to 300 tons of soda equivalent per day is usually approximately 8 ft in diameter and 170 ft high. There are stills of 500-ton capacity that are 10 ft in diameter, and stills of 700- to 750-ton capacity that are 11 to 12 ft in diameter. The 170-ft height includes the condenser and preheater section, the "free" still, and the "fixed" or lime still. The lime still usually has 10 to 14 plates, spaced $2\frac{1}{2}$ to $3\frac{1}{2}$ ft apart, and therefore it has a height of well over 40 ft. The lime still is usually made entirely of steel plate. It has large overflow boxes, and is provided with access doors to make possible removal of the scale, of which enough accumulates in 60 to 180 days to reduce seriously the capacity of the equipment. In some older plants, the lime still was much larger in diameter, and was equipped with mechanical agitators in an attempt to maintain the scale at a slower rate of growth. Such stills continue in use in the older European plants, but their high cost and their complexity make them obsolescent. Modern trends are to operate the equipment in such a way that cleaning is required as little as once a year (or even less frequently). This is achieved by better temperature control and also by the use of additives of the sodium aluminate types which affect gypsum deposition. Apparently, there are several sensitive ranges in

which hemihydrate and dihydrate of calcium sulfate tend toward or away from states of supersaturation.

The lime still is usually surmounted by the "free" part of the still, which is a cast-iron section either of the bubble-plate type or else tile- or coke-packed. Modern types of ceramic packing are being developed which permit shorter towers (see Absorption; Distillation) so that the latest designs of the free still include both the preheater and the free still in packed form, surmounted with a surface or tubular condenser.

The free still is usually the same diameter as the fixed still and of about the same total height or a little greater. The preheater section of a Solvay ammonia still consists of cast-iron tubed cast sections, which permit countercurrent preheating of the filter liquor. The filter liquor usually goes through the tubes, and is removed at three or four places along its path to permit venting of the evolved carbon dioxide. In the most modern stills this part of the apparatus is by far the most extensive, and the condenser that surmounts it is relatively small. In the older plants the condenser was large and the preheater comparatively small. The condenser also consists of cast-iron sections, similar to those of the preheater, except that cooling water circulates through the tubes instead of filter liquor. Some stills have bubble trays between each pair of cooling boxes, both in preheater and condenser, whereas other stills depend on the tube films and droplets of condensate to provide sufficient interphase contact.

Gas Compressors. A 500-ton-per-day soda plant requires gas compressors of about 3000 to 4000 hp to handle the suction on the kilns and to compress the gas into the Solvay precipitating towers. The most frequently used type for this purpose, until the mid-twentieth century, was horizontal, duplex-reciprocating equipment, generally steam-driven by a cross-compound steam engine. In some plants the reciprocating compressors are electrically driven. The construction of the gas end is preferably cast iron, with special types of valves and special lubricating devices to take care of the dirt and corrosiveness of the gas. However, more and more plants are installing centrifugal compressors, some turbine-driven, and some electrically driven with step-up gears. These are usually multistage machines using stainless steel rotating elements and shaft power of at least 1000 hp.

Substantially all other parts of a soda plant, such as the power plant, water-pumping facilities, electric generators, and control instruments, are standardized items analogous to those used in all process plants.

Economics

Although in 1945 the United States produced about 4.5 million tons of soda ash and this had increased to 5.4 million tons by 1960, the earlier figure represented nearly one-half of the world's production but the 1960 figure represents little more than one-third of the world's production. That change is partly explained by the fact that 1945, the first postwar year, was hardly typical for the industrial nations that had suffered much physical war damage and war's serious economic displacements. Also, between 1945 and 1960, the demand for chlorine grew much faster than for alkali, especially in the United States, and the resulting coproduct, NaOH, caused a greater displacement of soda ash in the United States than elsewhere.

The production cost of soda ash at the factory can best be inferred from the following ranges of consumptions, rather than in the currency of some particular

nation at some arbitrarily chosen time. The cost tends toward a minimum when the factory capacity is high; when the technical efficiencies and labor utilizations are high; and especially when sales keep the factory operating near its top capacity. The costs are at maximum in obsolescent small factories, especially those unable to keep sales volume up to a high fraction of the plant capacity. The largest factories are seldom the most technically efficient because, while growing to large capacity, they have tended to maintain obsolescent equipment and labor practices to avoid excessive capital retirement losses. As soda ash is always a large-volume operation, the incremental out-of-pocket costs are essentially only for fuels and manpower. The raw materials, salt and limestone, are usually produced under the direct operation and ownership of the alkali factory itself, and the costs, as shown in Table 2, appear essentially as labor and supplies.

The usual, or normal, unit consumptions can be taken as lying between the two extremes described above and are summarized quantitatively in Table 2.

The total of the cost factors given in Table 2 comprises "fob factory net cost"

Table 2. Soda Ash Production Cost Factors
(All data per 2,000-lb ton of Na₂CO₃ sold)

Cost factor	For technically efficient, fully loaded factory	For low-capacity obsolescent, lightly loaded factory
salt, tons	1.5	1.8
limestone, tons	1.08	1.4
ammonia, lb NH ₃	2.0	8.0
sulfide inhibitor, lb Na ₂ S	2.0	6.0
other raw materials and manufacturing supplies ^a		
kiln coke, lb	145	220
other fuels, mil Btu	5,500	9,500
direct operating labor, man-hours	1.0 ^b	3.8 ^b
factory supervisory labor, man-month	0.003	0.01
maintenance and repair labor, man-hour	0.7	2.8
maintenance materials, % of maintenance labor cost	50	120
depreciation, obsolescence and depletion ^c		
overhead items ^d		
sales expenses ^e		

^a Under this heading most manufacturers now include bags and barrels, car liners, and dunnage used in shipping; boiler feed water-treating chemicals; quarry explosives, etc. Less and less ash is being packaged, most (in U.S.A.) going bulk. Boiler waters and quarry conditions vary over too wide a range for a mean figure to have merit.

^b These figures include labor for reasonably normal limestone quarrying and transport by conveyor belt, cable road, or short-haul motor truck. If stone is purchased these labor figures could be reduced 20–30%. Routine chemical control operations are included, but "trouble shooting," technical development, plant engineering, and the like are included under "supervisory."

^c Practices under these headings vary widely. Tax laws in most countries tend to establish these matters, but the total of these items will be bracketed by a low of approximately 8% annually on \$20,000 per daily ton of capacity to perhaps 15% annually on \$50,000 per daily ton of capacity,

^d Under this heading the manufacturer usually includes all casualty insurance costs, medical, legal, and engineering expenses, research and development, local taxes and assessments, communication, etc.

^e This includes all direct costs of selling, operation of local sales offices, advertising, technical service to customers, freight equalizations, etc.

to which central office expenses, income taxes, interest on indebtedness, dividends, and profits are to be added to determine "price."

In common with most "old" industries, soda ash making has become less and less profitable in recent years; most new factories built since World War II have had to have some sort of subsidy or partial government support. Added equivalent soda ash capacity has become available without new investment as electrolytic plants have come into being. The price of soda ash has not advanced in keeping with added factory construction costs and fuel costs, as illustrated by Figures 7 and 8.

Location of Industries. Soda ash is a cheap bulk product. It can be manufactured profitably only where there is a favorable combination of raw materials and services close at hand and in areas offering relatively short hauls to "tonnage" consumers. Approximately 8 tons of brine, stone, and fuel are brought into the works for each ton of soda ash shipped out. Obviously, a factory must be located closer to its sources of raw materials than to its consumers. Salt is much less widely distributed than limestone, but the locations where the two are in commercial proximity are fairly numerous. In the U.S.A., the concentration of industrial market in the eastern half of the country, together with the tremendous economies effected by large-scale manufacture of soda ash, have combined to create the situation illustrated on the map (Fig. 4). In Europe, on the other hand, where there are many more national borders to affect the situation with respect to import and export duties, and where competition may take place at the cartel table rather than at the purchasing agent's desk, there are many more plants and they are generally of smaller capacity. The map (Fig. 4) shows the geographical location of the operating companies in the U.S.A., and shows also the approximate freight boundaries along which soda ash can be received from either of two suppliers at the same freight cost. Figure 5 gives some indication of capacities for soda ash manufacture in the principal countries of the world.

Requirements for Ammonia-Soda Manufacture. The materials that an ammonia-soda factory must have are listed in the order of the usual cost of each item per ton of soda ash produced: (1) fuel, (2) labor, (3) limestone, (4) salt, (5) water, (6) ammonia, (7) factory supplies. Every item in this list, with the exception of ammonia (which is a small item), is widely available, although not always in the densely populated parts of the world where the pursuits of civilization afford the potential alkali market. The salt, coal, water, and limestone are the important items in determining the location of an ammonia-soda plant. This does not limit the location of an alkali plant too sharply, because limestone is widely distributed and sea salt serves for the manufacture of ammonia soda in the absence of any cheaper form. Generally the salt for the process is obtained from underground beds of this mineral. Locations where underground strata of salt are available for this process are usually extensive—for example, in the United States the basins of Lake Erie and Lake Ontario overlie tremendous deposits. Along the Gulf Coast of Louisiana and Texas there are "salt domes." Somewhat smaller isolated deposits of salt exist in a few valleys of the Appalachian Mountains, and far western states have outcropping deposits. Other great areas of salt in the U.S.A. are in the less populated regions between the Rocky Mountains and the Mississippi River, where the lack of a market for soda ash has so far prevented exploitation for this purpose. The other important requirements, cheap fuel and capable labor, are, of course, available in all industrialized areas where there is a significant market for soda ash and its allied products.

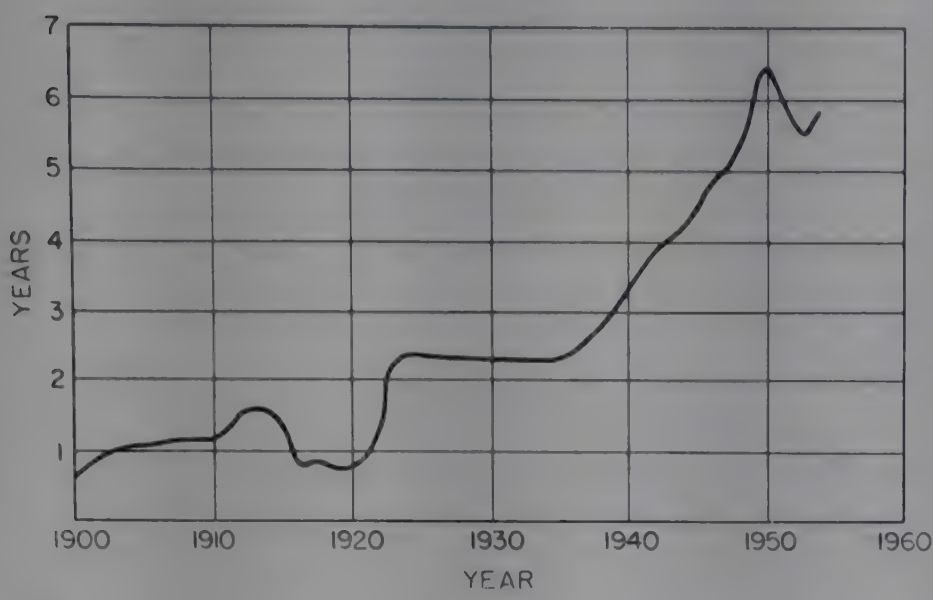


Fig. 7. Soda ash factory construction costs showing years required for ash sales at bulk list price to equal factory replacement cost.

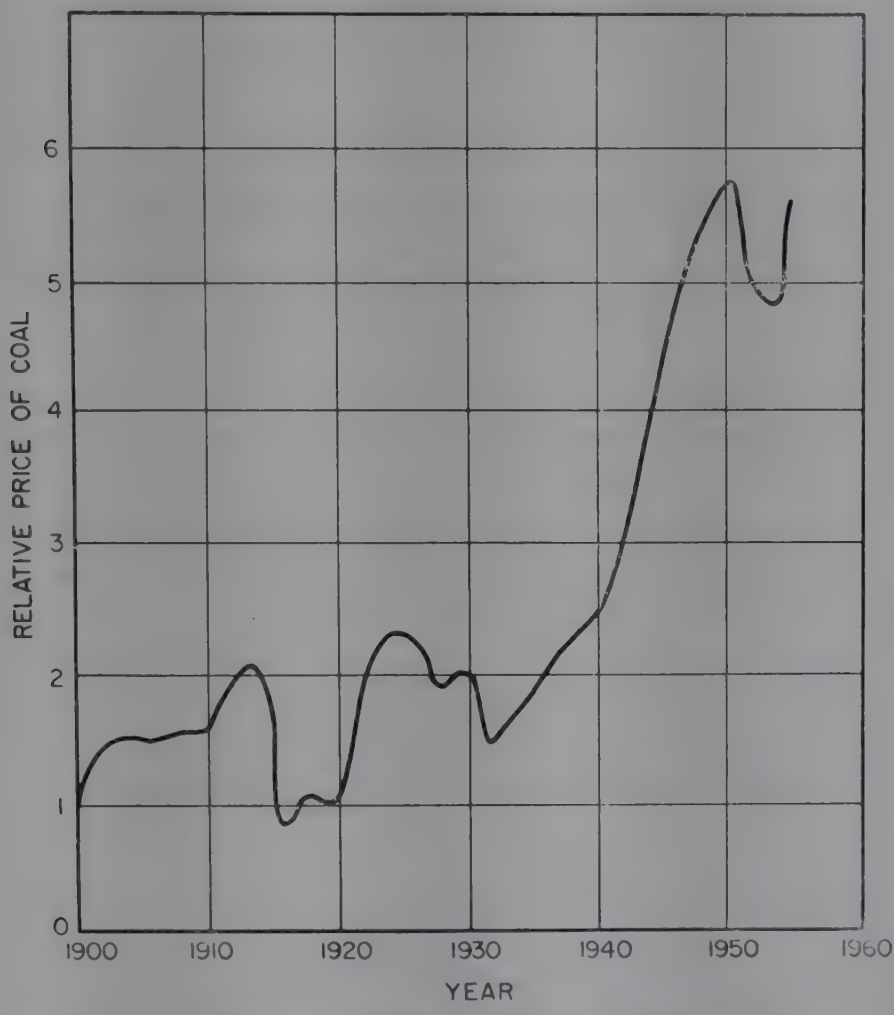


Fig. 8. Trend in cost of coal in terms of soda ash. The relative cost of coal was determined by dividing the dollars per ton of coal by the dollars per hundredweight of bulk soda ash.

Probably the most important requirement for a soda ash plant is a large market. The process and the equipment effect marked economies under large-scale operation; hence, the chance that a small plant, less than 500 tons per day, could compete within the United States is almost zero. Small factories in remote sections, where a concentrated market might develop are, of course, a possibility. Smaller factories have been built since 1945 in countries with nascent industrialization, although none has been undertaken where market studies predict less demand than 200 tons per day.

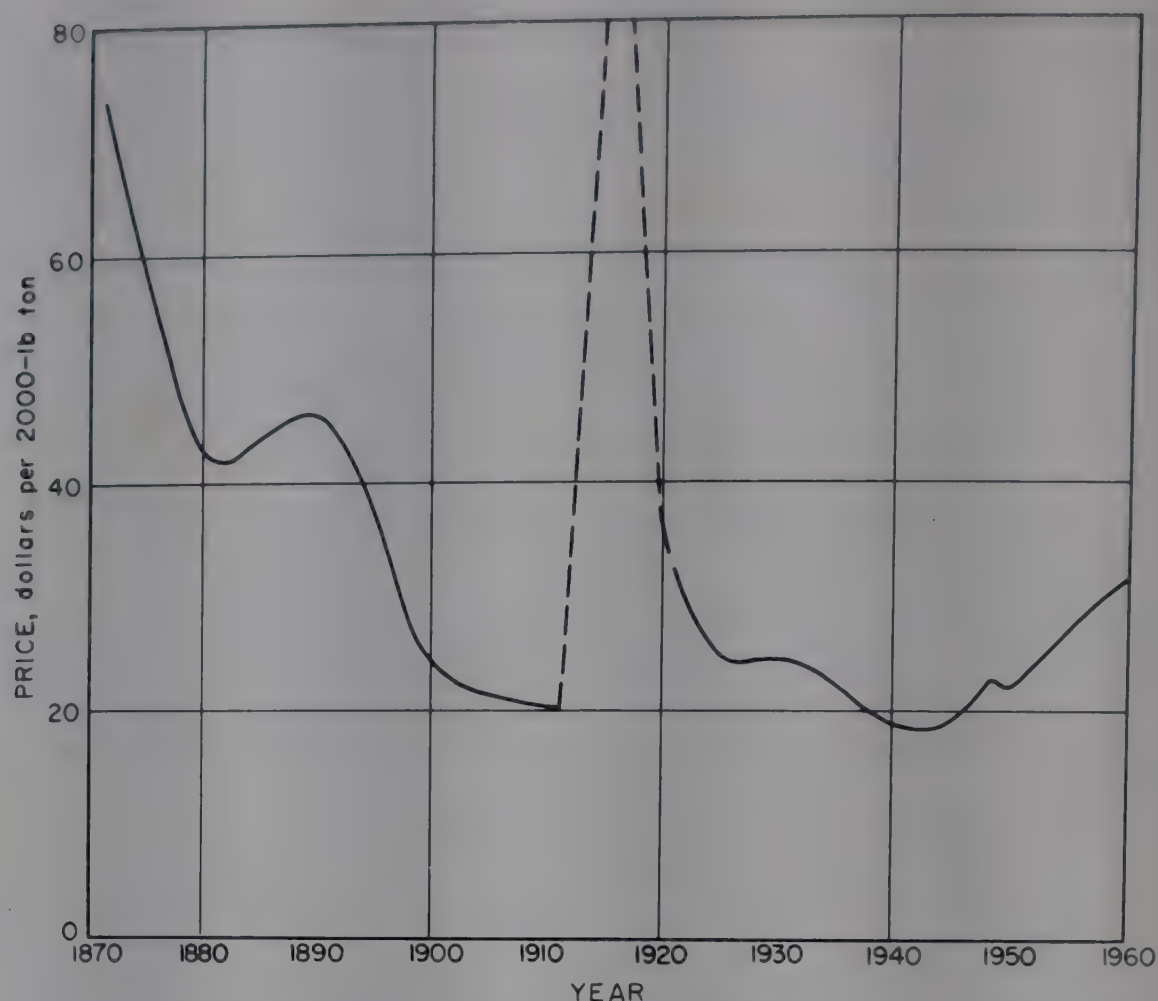


Fig. 9. Price history of soda ash.

Interrelation with Other Industries. Soda ash is an important raw material in many industries. The glass industry is the principal customer for soda ash, as such, and controls, more or less directly, many of the world's producers. Caustic soda is the form in which most of the alkali is used in the soap industry, but since considerable soda ash is used in the manufacture of special soaps and detergents, some foreign soap manufacturers convert soda ash to caustic within their own soap plants. Glass and soap are manufactured in many places in the U.S.A. In general, it may be said that no important industries consider proximity to soda ash plants vital to their operations, but during World War II, two of the larger magnesium metal plants were built at soda works because (among other reasons) of the availability of NH_4Cl for decomposing dolomitic lime.

Factors Controlling Demand and Price. The history of quoted prices of light (ordinary) soda ash is shown for the U.S.A. in Figure 9 from the beginning of Solvay operations. The minor rise since 1950 represented less of a revenue increase for the manufacturers than might be inferred. The intermediate density grade, sold at the price of the light product, took over a very large part of the market for dense ash which had been sold at a \$2.00 premium over light ash.

Prices elsewhere in the world reflect local costs of salt and fuel principally. For example, salt in Japan is very expensive since less than half of it is made locally and that by a very expensive solar process. The remainder is imported from long distances. However, the conversion costs in Japan are actually lower than elsewhere because of profitable low-cost local fuels and efficient local labor. The newest European plant, in the Netherlands, has a very favorable salt situation and a not too unfavorable limestone situation, and produces at costs comparing favorably with the

largest American plants using partially obsolete equipment. At all times, and particularly during World War I, much soda ash sold for considerably lower prices than indicated by Figure 9. This is due to the long-term contracts with substantial discounts, which prevail in the industry. The published prices reflect warehouse operations of distributors, usually only a minor fraction of the total.

Uses

The uses of soda ash in the United States, as illustrated by Figure 2 for the 30 years ending in 1960, have been about as follows: glass, up from 25 to 35%; caustic soda, from 35 down to less than 10%; sodium silicates, 5%; sodium chromates, 2%; sodium bicarbonates, from 5 down to 2%; cleansers, 3%; soap, from 12% down to less than 1%; phosphates, from 4 up to 12%. These changing patterns in the uses of soda ash, as represented in Figure 2, are not fully appreciated without bearing in mind the rapid rise in total soda production during these three decades (1960 production was $2\frac{1}{4}$ times that of 1930). "Other chemicals" and "Miscellaneous" always tend to increase faster than other soda ash consumption categories, a strong symptom of the increasing diversity of the enlarging market for these basic chemicals. The most significant changes of the last 30 years or so have been the decreasing use of soda ash for conversion to caustic soda because of the rapid rise of coproduct caustic from the chlorine industry. The increase in sodium phosphates and decrease in soap reflect the increased use of phosphatic detergents, especially in laundering, and the increased use of nonferrous metals essentially represents increased use of aluminum metal.

By-Products

Calcium Chloride. (See also Calcium compounds.) The principal coproduct that has been mentioned thus far is calcium chloride. Relatively few soda ash factories produce "finished" calcium chloride, and those that do prepare for sale only a small part of the total amount available in the still waste. Calcium chloride is used on roads, as a dust abater on gravel, and as a deicer on hard-surfaced highways. It is used in cement products, for freezeproofing and dustproofing coal and coke, in refrigeration brines, and as a drying agent.

In the finishing of calcium chloride, the still waste liquor is given a preliminary settling and then usually a treatment with barium chloride. This precipitates most of the sulfate, which would otherwise give fouling trouble in the evaporators used to concentrate the solution. Some factories treat the distiller waste with carbon dioxide gas, which precipitates free lime and favors the sedimentation of the sulfate. The clarified liquor is then evaporated in multiple-effect tubular evaporators to approximately 40 to 42° Bé, at which concentration most of the common salt, NaCl, is precipitated. The salt is separated, most often in centrifuges, and the remaining solution is concentrated in single-effect evaporators to the equivalent of the $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ condition. This solution is then flaked on ordinary flakers, and these flakes are dried in a rotary dryer, giving a reasonably stable $2\text{H}_2\text{O}$ flaked product, sold as 77–80% calcium chloride in paper bags. A small amount is carried to the anhydrous condition. Another large part of the product is cast into single-trip steel drums and sold as 73–75% calcium chloride. The common salt, which is centrifuged out of the solution, is usually washed away because its high calcium content makes it expensive to purify for reuse in the ammonia-soda or adjacent electrolytic operations.

Refined Bicarbonate and Sesquicarbonate. (See also Sodium compounds.) Practically all soda ash factories manufacture refined sodium bicarbonate from the soda ash. In the United States, from 1930 through 1960, the consumption has been about 170,000 tons per year, showing a drop of per capita demand from almost 3 lb in the early 1940's to less than 2 lb in 1960. This product is used principally in the baking industry for baking powders, other antacid powders, and for medicinal purposes. A growing use is in fire extinguishers.

At alkali factories, refined sodium bicarbonate is made by carbonating a pure soda ash solution with purified kiln gas. The solution is made either by redissolving the final soda ash or else by "wet calcination" of a crude bicarbonate slurry. The precipitated refined bicarbonate from the recarbonation is filtered as in the ammonia-soda process and predried by centrifugation; the final drying is carried out in moderately heated (below 100°C) air-swept dryers of various types. It is also air-graded to size and sometimes screened and bolted. The filtrate from the filters is used to dissolve more fresh soda or to repulp the slurry of crude sodium bicarbonate being fed to the stripping stills (wet calciners). Some of the product is packed into small boxes, but most of it is barreled or bagged for the trade.

By the proper combination of carbonation and concentration, sodium sesquicarbonate, $\text{NaHCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$, is produced in a few alkali factories. This alkali is used in bath salt manufacture and in proprietary laundering compounds.

Dry Ice. (See also Carbon dioxide.) At some soda ash factories, liquid carbon dioxide and solid carbon dioxide (dry ice) are manufactured from the excess kiln gas. Liquid carbon dioxide is used for carbonated waters, fire-fighting equipment, and has been developed as a coal-mine explosive. Dry ice is used principally as a refrigerant in the preservation of food products and in the retail distribution of frozen products; hence most of it is made near concentrated local markets from coke-burning boiler flue gases.

Caustic Soda. An important end product of the alkali industry is caustic soda. The manufacture of caustic soda is discussed in the following section, "Sodium hydroxide," p. 740.

Ammonium Chloride. Ammonium chloride is the principal salt present in the mother liquor from the crude sodium bicarbonate filtration. For quite a number of years small amounts of ammonium chloride have been put on the market by a few soda ash makers. However, this has been on a small scale because most of the demands for ammonium chloride are low-tonnage. It is used in wet and dry cell electric battery manufacturing and as a pickling agent in galvanizing and tinning operations. A big potential use of NH_4Cl , overshadowing the total of all other uses, is as a fertilizer. For the smaller uses, production has come from the concentration of the CO_2 -free mother liquor.

Coproduction of soda ash and ammonium chloride has been practiced at Oppau in Germany for many years; the first patent, assigned to Schreib, is dated 1872. The scale of operations at Oppau hardly ever exceeded some 100 tons per day. The operations, up until World War II, were varied, and are described in reference 1.

The idea of getting a better utilization of the common salt than the 65–75% of the standard Solvay cycle has long appealed to many chemists in the industry. Most of the early schemes described in the literature were unsuccessful in separating out a satisfactory yield of ammonium chloride which was pure, because a thorough knowledge of the heterogeneous equilibria (the gaseous phase as well as the solution and

crystal phases) was lacking. The most complete published data are those of Reinders and Nicolai (8). Their studies show the important effect gaseous ammonia has on the solubilities of the salts in solution.

In Japan these relationships were thoroughly reinvestigated, and since 1955, the Asahi Glass Company has operated the first really substantial factory for such co-production (9). The success of that operation, coupled with the fact that NH_4Cl is a favorable fertilizer for many of the big crops of rainy climates, has brought about the prediction that within a few years, all the Japanese soda ash factories will shift over to the NH_4Cl - Na_2CO_3 cycling process.

Figures 10 and 11 help to elucidate the following description: The ammonia is dissolved in the bicarbonate solution (B solution) left after the separation of the sodium bicarbonate from the slurry coming from bicarbonating towers, quite similar to those used in the conventional Solvay process.

The total amount of ammonia necessary for the whole process is added at this stage and this is the most vital point of the newly developed process as it is this procedure that prevents codeposition of sodium bicarbonate in the subsequent ammonium chloride precipitation stage.

In the Schreib process and its modifications, either ammonia was not added at this stage or it was added only in a comparatively small quantity, which made it impossible to increase sufficiently the solubility of the sodium bicarbonate and made the codeposition of sodium bicarbonate with ammonium chloride in the ammonium chloride deposition stage uncontrollable. To enable a stable operation, it was necessary to perform a detailed phase rule study of this system using aqua ammonia as a solvent, and to define the optimum operating conditions.

The ammoniated solution (A solution) obtained by the addition of ammonia to the B solution is cooled to $5\text{--}25^\circ\text{C}$ and common salt is added in solid form. The salt dissolves and ammonium chloride precipitates. The mother liquor obtained after separation of the ammonium chloride (C solution) is warmed by heat exchange with the A solution and sent to the carbonating towers.

The C solution already contains some sodium bicarbonate and therefore no washing tower operation, as in the conventional Solvay process, is performed. However, inasmuch as the making towers have to be cleaned periodically, either A or C solution is used for that purpose. The change in the liquor composition of this operation is shown in Figure 11.

Point b is the B solution or the composition of the mother liquor after separation of the NaHCO_3 . With the addition of NH_3 it advances on line bC and reaches point a. After addition of the NaCl and cooling, the composition advances on line aA and reaches point d. At point d the NH_4Cl precipitates and the mother liquor obtained after separation (C solution) reaches point c on line Bd. By blowing CO_2 into c, the liquor composition reaches point e on the line Be which is vertical to the plane ABCD, and NaHCO_3 precipitates. The mother liquor after separation of the sodium bicarbonate returns to point b on line Fe. It is necessary to define the operational conditions which would permit starting from a B solution of a given composition, and after going through the various operational stages shown in Figure 11, permit return to the B solution while securing, all through the cycle, the necessary balance of the components (9,10).

There are significant differences between the equipment of the conventional Solvay process and the ammonium chloride-soda ash cycling process. With the latter

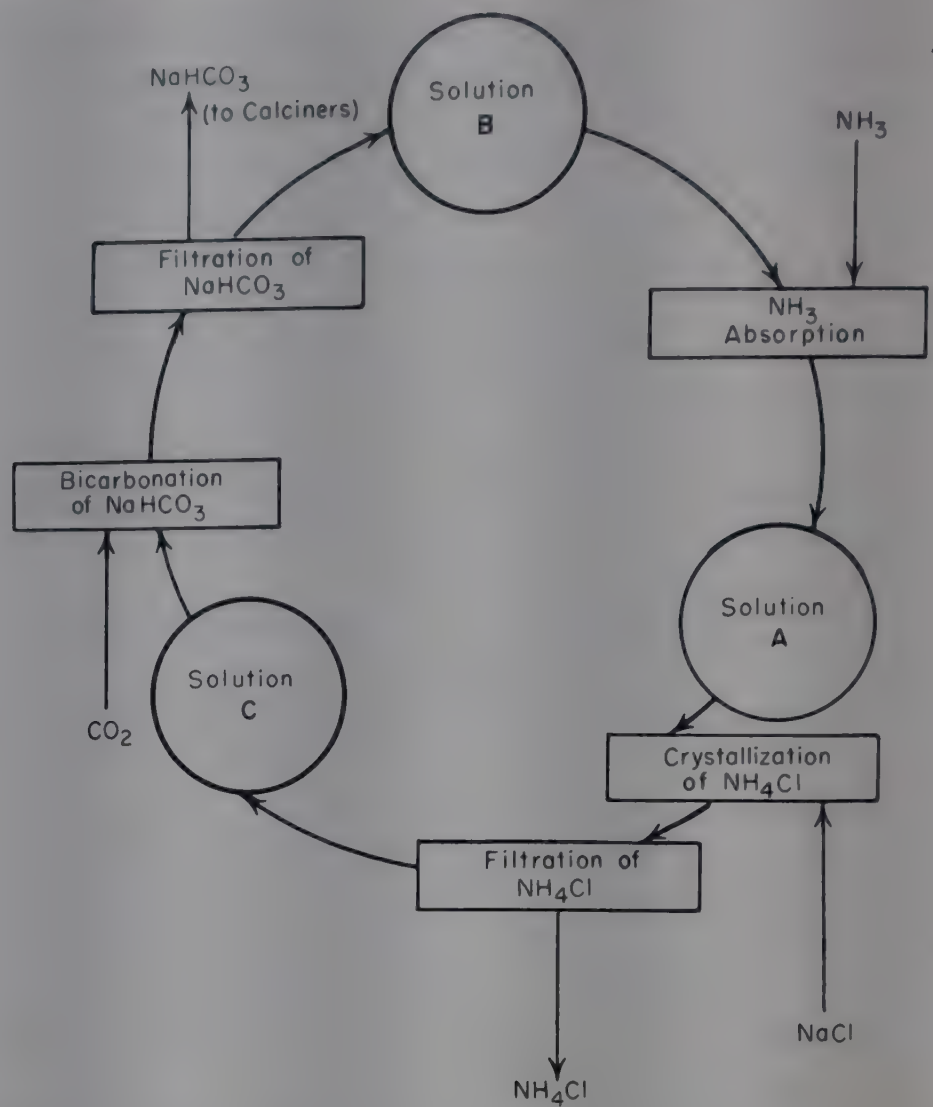


Fig. 10. Process diagram of ammonium chloride-soda ash coproduction.

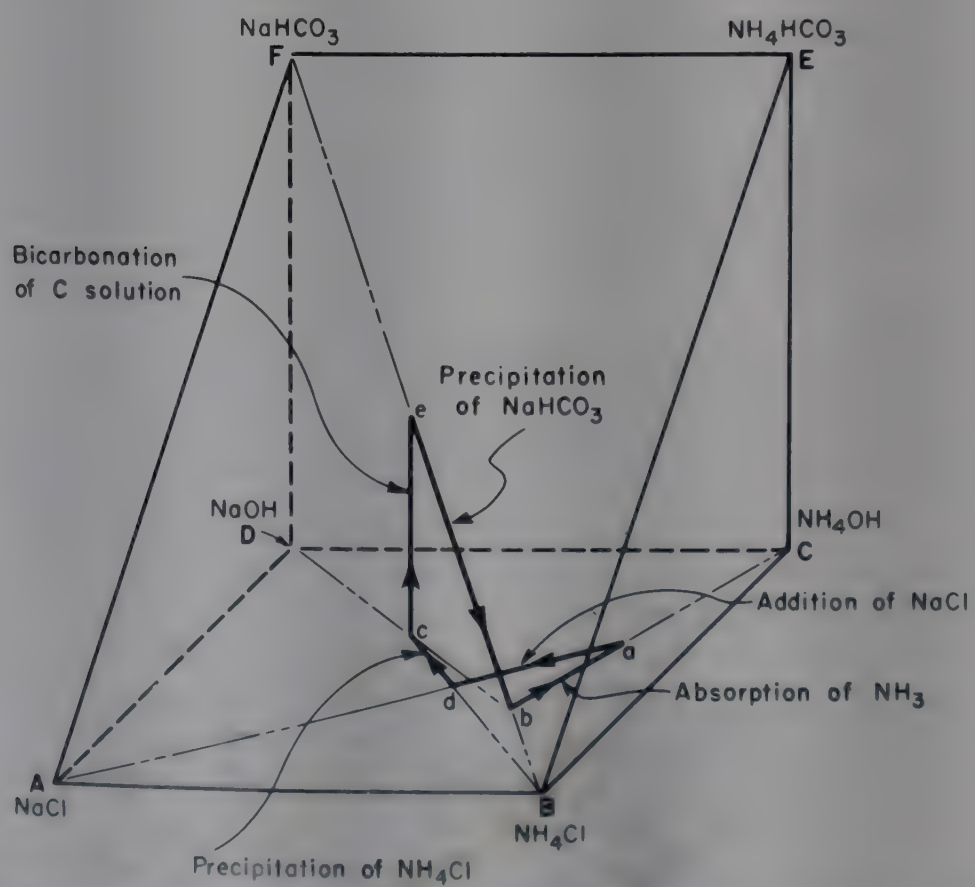


Fig. 11. Operating lines of NH₄Cl-Na₂CO₃ cycling process, represented by three-dimensional diagram.

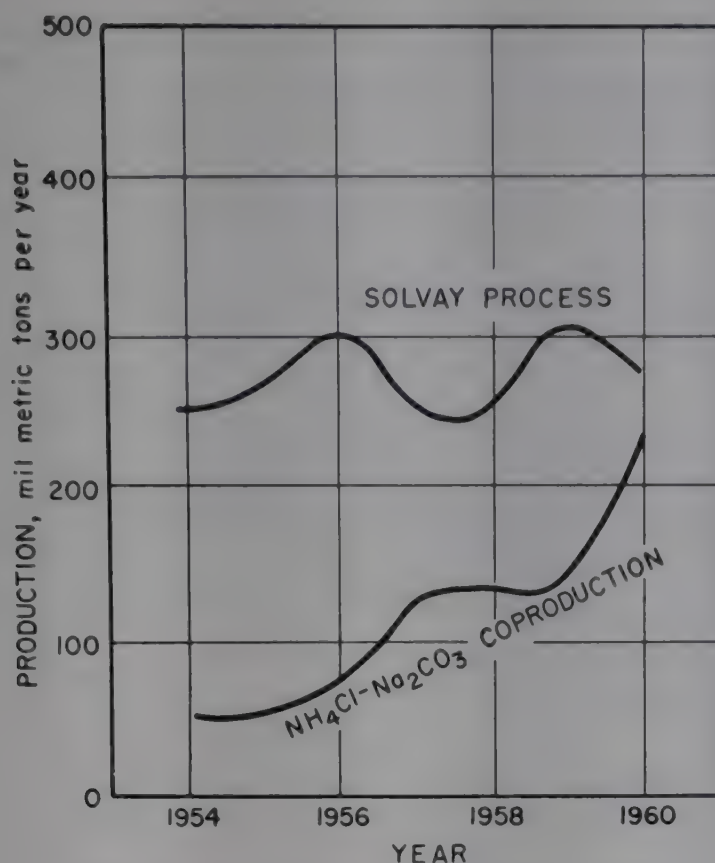


Fig. 12. Production of soda ash in Japan.

there is no ammonia recovery and therefore no distillation tower; no milk of lime and consequently no lime kiln. Further, since the salt is used in solid form, the brine purification system, with its big settling tanks, disappears.

On the other hand, the ammonium chloride-soda ash cycling process requires, unlike the regular Solvay plant, equipment to wash the solid salt, and for the ammonium chloride production, crystallizers, filters, dryers, and cooling equipment. In addition, an ammonia source is required which preferably would also supply the CO_2 for the bicarbonation. Further, inasmuch as the liquors containing ammonium chloride are extremely corrosive, the materials of the equipment must be special cast irons and properly selected plastics. Because the mother liquor is circulated, it is necessary to give special attention to the balance of the water through the system; a close control of the waters coming into the system, such as the wash waters for the sodium bicarbonate and ammonium chloride, has to be maintained.

As a fertilizer, ammonium chloride can be used in ordinary cultivation in rainy climates in the same way as ammonium sulfate is used. In dry climates, it can be used effectively for quality improvement of cotton and other textile plants. It is said to be entirely unusable for tobacco growing.

In Japan, ammonium chloride is used extensively for rice and other grain crops, vegetables, and fruits. In many cases it has been shown to be more effective than ammonium sulfate for paddy field rice, and is clearly superior when used in worn-out paddy fields.

Figure 12 shows the trend in production of soda ash in Japan by the Solvay process and by the $\text{NH}_4\text{Cl}-\text{Na}_2\text{CO}_3$ coproduction method.

Where natural gas, solid salt, and the other facilities for both NH_3 and Na_2CO_3 manufacture are at hand, this process should prove attractive, and could be the incentive for the development of widespread use of NH_4Cl as a fertilizer. The rice-wheat cycle of Japanese agriculture, together with the high cost of salt in Japan,

makes NH_4Cl especially appropriate there. It might also be used on a large scale elsewhere, but the complex and changing competition of other fertilizers is such that the possibilities are not clear.

Recent Developments

Change of Process. The most significant change in the essentials of the ammonia soda process in recent decades was the widespread adoption of the steam-heated calciner which had been in use since the 1930's. Another significant change, which has been more recent and as yet applied to very few factories, is the use of dry lime for ammonium chloride decomposition. Except for these, there have been no radical changes in the process since Ernest Solvay had it profitably developed around 1900. But such a statement is analogous to the statement that the automobile of 1960 is in all essentials similar to the automobile of 1905. Detailed improvements in the manufacture of ammonia soda have taken place throughout the lifetime of the industry, and have been of such an intimate and complicated nature that any adequate description of them is beyond the scope of this presentation. Modern materials of construction and modern methods of control are all quickly applied to the process to make its product purer and more uniform and to reduce the cost of production.

Although it is technically possible to make soda ash from the lowest grades or more impure kinds of commercial salt and limestone, the industry has gradually learned that the purest and most uniform, structurally sound limestone and thoroughly purified and saturated brine are essential to reasonably trouble-free operation, and that "troubles" generally cost a lot more than could be saved by the use of lower quality raw materials. Soda ash, being so basic a product, purchased almost entirely by manufacturers necessarily keen on quality control, has been subject to ever more stringent quality specifications. There has been a continuing decrease in the amount of common salt tolerated in the finished product. Although it may appear that 99.8% Na_2CO_3 is not much purer than 99.3% Na_2CO_3 (approximately the 1960 and 1910 values), it has in fact meant a big difference to the alkali producer. Much more difficult in recent years have been the several types of empirical tests for "specks" representing Fe_2O_3 and other nonhomogeneous contaminants. Soda ash is so extremely white that when such specks are counted in the field of a microscope the difference between "acceptable" and "surely rejected" represents a difference of impurity content, for which it is impractical to analyze by chemical means.

Natural Soda. The rapid increase in the amount of "natural" soda ash on the market since the end of World War II has, in the U.S.A., come about principally by the opening up of mines for the exploitation of the sodium sesquicarbonate deposits in the Green River Basin in southwestern Wyoming. There also has been some increase in the carbonation of natural alkali brines at both Searles and Owens Lakes in California. Both of these operations, of course, have followed the westward trend of general industry.

Mineral forms of soda are few in number, and the only one with present economic importance is the sesquicarbonate, or trona: $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$. In addition to the solid deposits of that hydrate, there are a number of salt lakes from which a brine, reasonably strong in Na^+ and CO_3^{2-} ions, can be pumped and processed to produce soda. Finally, some soluble salt mining and refining operations (such as for potash) do actually, or can potentially, put some soda on the market.

There are a few primitive operations for leaching trona out of desert sands in low-lying dry lakes, but these have only restricted local significance. The natural soda operations, which are a substantial competitive factor in the world alkali market, are (1) deep mining and surface refining in the Green River Basin of southwestern Wyoming; (2) hydraulic dredging and calcining at Lake Magadi in Kenya, East Africa; (3) brine carbonation and subsequent processing at two dry-bed lakes in California and at another in Mexico. Possibly there are others of comparable significance in Asia, but as shown in Figure 3, the sum total is estimated to be less than 7% of the world's soda ash, and is hardly more than 3% of the world's Na_2O .

The total resources of the Green River deposits are estimated to be 28 billion tons of trona (20 billion tons of soda ash) or about as much as the whole world could use in 1000 years at the 1960 rate. The trona lies in beds separated by shale and from 1000 to 2500 ft below the surface. The strata of trona vary from inches to perhaps 40 ft in thickness, the total of which at any one location is from a few feet to over 100 ft. The mineral is mined in the dry, crushed, purified by recrystallization, and converted to soda ash by calcination.

At Searles and Owens Lakes in California, some soda ash coproduct is made from potash operations and some brines are carbonated with flue gas; the resulting bicarbonate is filtered and calcined.

At Lake Texcoco, near Mexico City, an alkali brine is concentrated by solar evaporation, then carbonated to precipitate bicarbonate; the filter cake is calcined to soda ash.

At Lake Magadi near the Kenya-Tanganyika border, trona as a solid phase is being dredged hydraulically and, with very little purification, is being calcined to a dense soda. Sodium fluoride is the only significant impurity not found in usual sodas. The resources of this region are said to be tremendous, as a similar, much larger lake lies just to the south in Tanganyika.

Need for Further Development. The consumption of fuel and of salt in the soda ash industry are still considerably higher than is theoretically possible. Important reductions have been made along the line of modernization of power plants of the "topping turbine" style, whereby electric power for chlorine manufacture is available from the same fuel as is required for ammonia-soda manufacture. Also in the last two decades the substitution of steam-heated for externally fired calciners has reduced coal consumption. Many soda factories have changed over from coal to fuel oil and in some cases to natural gas, and from these changes the total heat input per ton of soda has, if anything, gone up, but the dollar cost per ton has gone down.

Laboratory explorations for better salt utilization (it is hardly over 65% efficient on an industry-wide basis) show that improvement is technically possible, but the very low "incremental" brine costs, together with the rise of the electrolytic process, discourage expenditures for developmental work.

Of much greater potential importance to the ammonia-soda industry than improved salt and fuel utilizations would be knowledge on how to build cheaper factories, or smaller ones at a lower cost per ton of capacity. If the industry had the know-how to build a soda ash factory at a capital cost one-third less than today's estimates, it would be equivalent to having the engineering know-how to wipe out the fuel cost entirely. The authors and their collaborators have seen no promising suggestions as to what direction such research should take.

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SODIUM HYDROXIDE

Sodium hydroxide, NaOH, formula weight 40.01, is a white deliquescent solid. It is corrosive to the skin and this property gave it the name *caustic soda*, a term widely used in industry. Caustic soda is very soluble in water and is strongly alkaline; hence, it is highly reactive and accordingly a very useful chemical. Mp, 318.4°C; bp, 1390°C; density at 20°C, 2.130 grams/ml; heat of fusion, 40.0 cal/gram. For solubility in water see Figure 1. Figures 2 and 3 give data on the boiling points of sodium hydroxide solutions. The boiling points of aqueous solutions of sodium hydroxide, saturated with sodium chloride, are industrially important because such solutions are encountered in evaporating diaphragm cell liquors, and also in several industrial uses of the material. For either set of curves, the boiling point at any pressure is obtained by reading to the Dühring lines from the boiling point of water at the same pressure. Figure 4 gives thermal properties of anhydrous sodium hydroxide, and Figure 5 is a simplified version of the precise and valuable determinations of the thermal properties of sodium hydroxide-water solutions made at the University of Michigan.

INDUSTRIAL HISTORY

Solutions of caustic soda (more correctly, solutions of NaOH plus Na₂CO₃) have been made ever since soda was commercially used, certainly since before the middle of the eighteenth century. Throughout the first half of the nineteenth century, such solutions were made by soapmakers, wool scourers, bleacheries, and papermakers for use in their own plants. The development of a shippable solid product probably dates from 1853 by the Leblanc sodamakers in Lancashire in England. It was made from the so-called "red-liquor" (the caustic mother liquor) by batchwise lime reaction, chemically no different from the lime-soda process of the mid-twentieth century. During the 1870's and 80's, there was a spate of development, reflected in numerous improvement patents. The Loewig (ferrate) process and the Bacon (strontium)

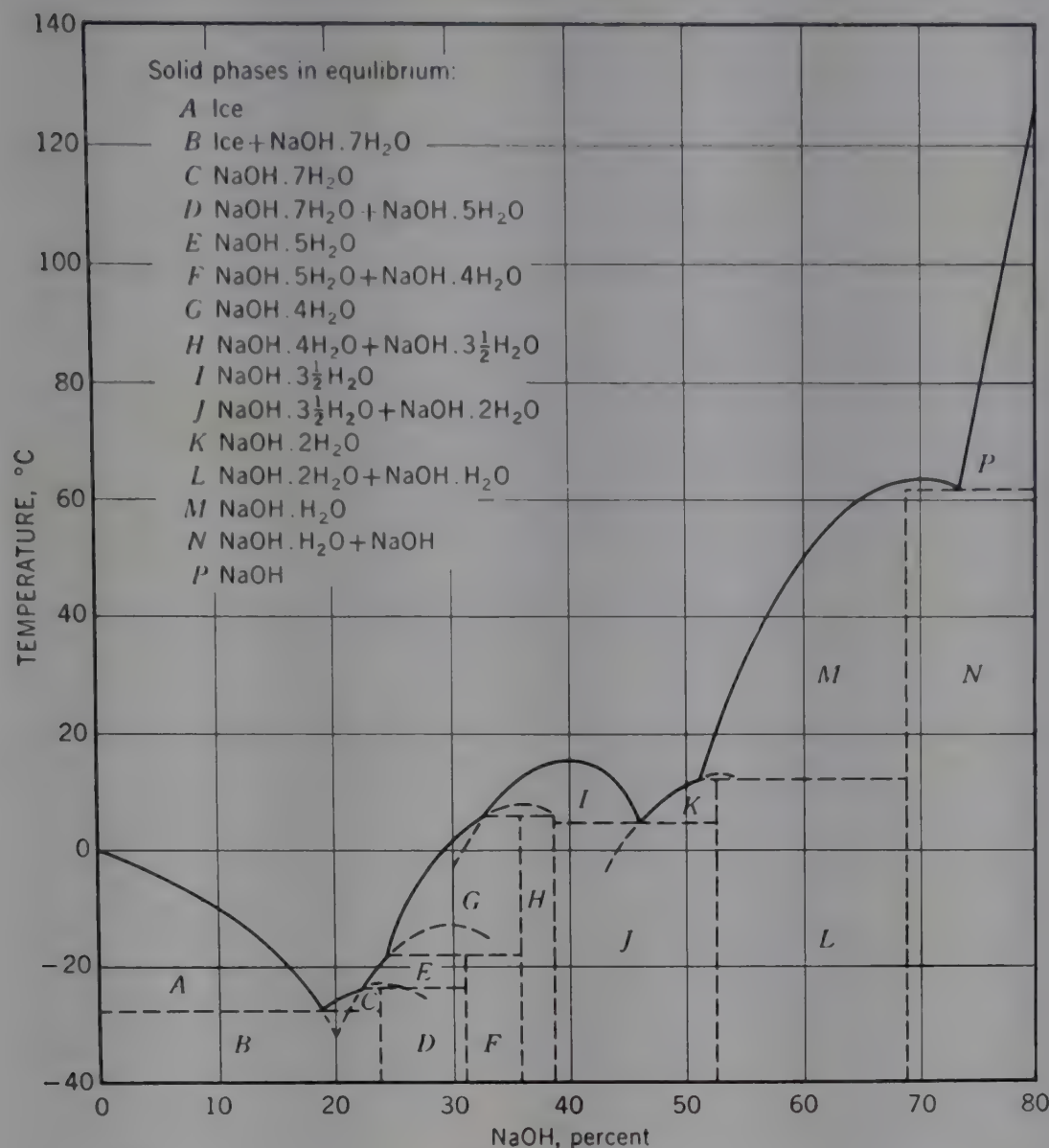


Fig. 1. Freezing point-solubility for system NaOH-H₂O (1).

process were patented in 1882 and 1897, respectively. The former failed to reach profitable operations and the latter seems never to have been tried on a truly commercial scale. The continuous lime processes were the only ones in important use during the early years of the twentieth century.

Table 1, p. 669, indicates that caustic soda ranks high in both tonnage and value among the important industrial heavy chemicals. Since 1925 it has grown more slowly than its associated product, chlorine, but it still leads chlorine by a small margin in both value and tonnage. Until shortly before World War I, the amount of caustic soda reaching the market as coproduct of chlorine was almost negligible compared to that made from soda ash by the lime reaction. The lime-soda process caustic exceeded electrolytic caustic in tonnage until just before the beginning of World War II. Since 1940, the electrolytic caustic reaching United States markets has exceeded the lime-soda caustic, and by 1962, the latter had almost disappeared. Figure 2, p. 709, shows that the uses of soda ash for conversion to caustic soda dwindled from about 27% in 1930 to about 6% in 1960. In 1925 electrolytic alkali was less than 6% of the total equivalent alkali consumed. Since then this percentage has steadily risen until in 1960 electrolytic alkali accounted for well over 50% of the total sodium alkali consumed in the United States. In a few individual countries of Europe where the diversity of industry has changed less than in the U.S.A., this figure may be higher. For the western European region as a whole, somewhat less than 50% of total alkali

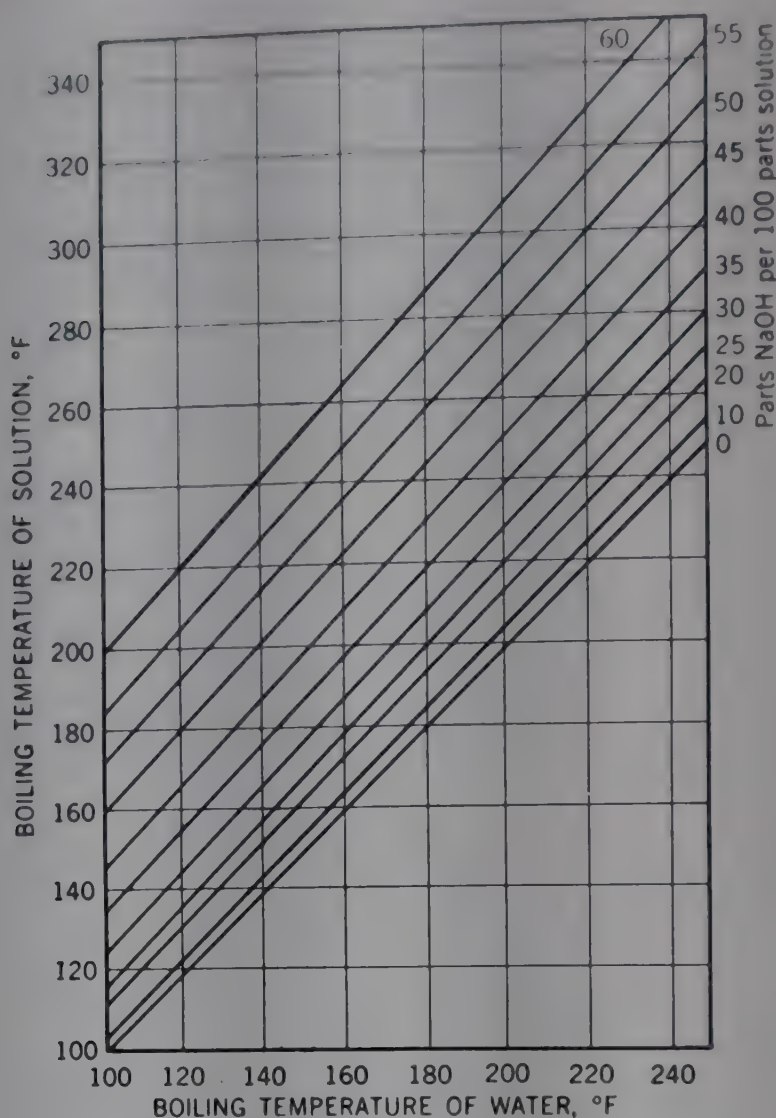


Fig. 2. Dühring lines for solutions of sodium hydroxide in water (2).

was being made electrolytically in 1960, although the fraction was climbing rapidly. Thus the increasing demands for chlorine had, by 1960, seriously cut the lime-soda process for caustic, where they had not already completely displaced it.

The causticization of soda ash with lime, and the electrolytic production from common salt completely overshadow any other process for making sodium hydroxide. The causticization of soda ash with strontium has been studied, because of favorable solubility relationships, but has not come into use. Some years ago endeavors to modernize and develop the Loewig process for caustic soda (which dates from the Leblanc era) led to the conclusions that the equipment involved so high a capital investment that the process, although thermodynamically sound, would be commercially unprofitable. In the Loewig process, soda ash was sintered in a rotary furnace with iron oxide, and the clinker of $\text{Na}_2\text{Fe}_2\text{O}_4$ was digested in water from which concentrated caustic soda was directly decanted, leaving iron oxide sludge which was then reprocessed. The process was never revived; even though equipment developments since it was last studied might have made it more attractive, the caustic consumer's tolerance of iron contamination has been drastically reduced.

The lime-soda process for the production of dilute caustic, which is rapidly declining in volume, will be discussed, after which the concentration of caustic liquors, both from the electrolytic and the lime-soda processes, will be described in somewhat greater detail.

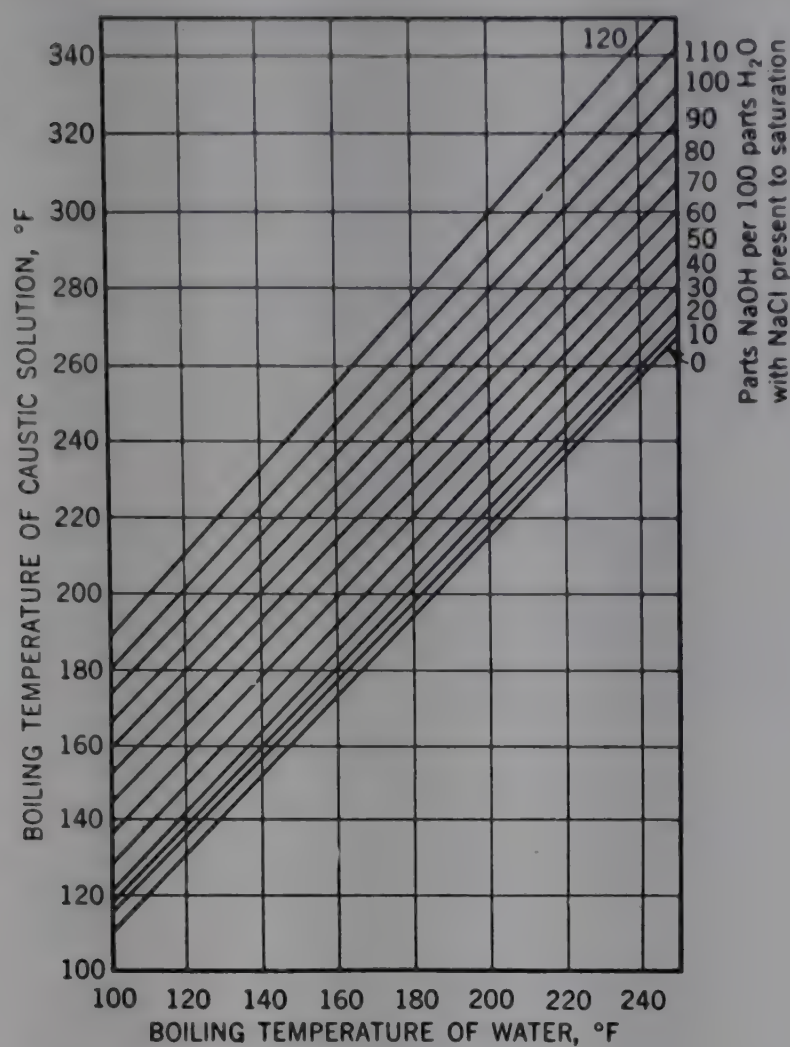
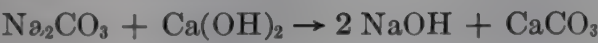


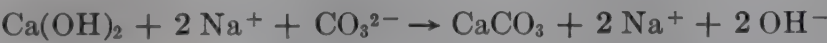
Fig. 3. Dühring lines for electrolytic caustic solutions (3).

Lime Processes

The well-known causticization reaction,



depends upon the fact that calcium carbonate is almost insoluble in water. The equation can also be written,



Since the calcium hydroxide and the calcium carbonate are present in solid form, their activities are constant and can be included in the equilibrium constant for the reaction, which then becomes

$$K = \frac{[\text{OH}^-]^2}{[\text{CO}_3^{2-}]}$$

The value of K , and hence the percentage conversion, is only slightly influenced by temperature because the heat of causticization is small; however, the speed of reaction is improved at higher temperatures. In the equilibrium equation, the concentration of the hydroxyl ion is squared and the concentration of the carbonate ion is in the first power; therefore, the more dilute the solution, the greater is the ratio of hydroxyl to carbonate ions. Thus, the percentage conversion is favored with more dilute solutions, but evaporation costs are increased with more dilution. In practical operation, the optimum integration of the two costs is met by producing a clear solution containing 10–11% NaOH, and 1.4–1.5% Na₂CO₃, corresponding to some 90–91% conversion of soda. The causticization equilibrium is illustrated by Figure 6.

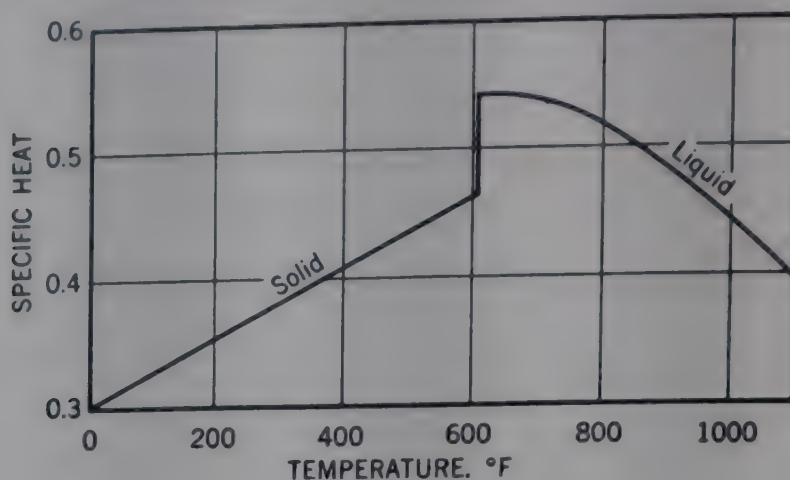


Fig. 4. Specific heat of anhydrous sodium hydroxide.

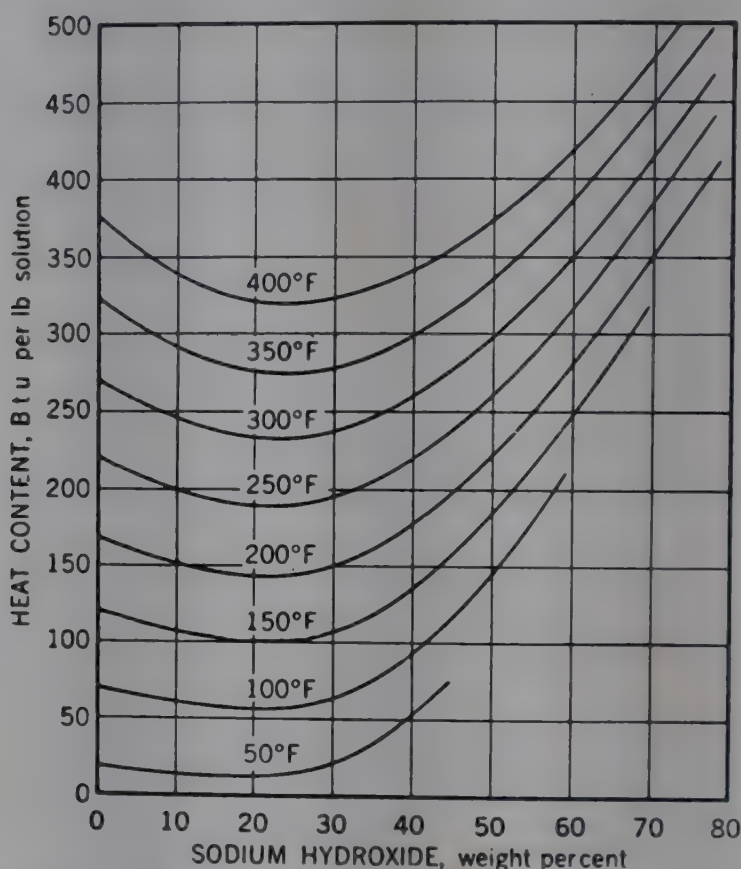


Fig. 5. Heat content of caustic soda solutions (2).

In most causticizing plants, the lime was slaked and the soda ash was separately dissolved with some of the dilute caustic liquors resulting from the succeeding mud washing, evaporation, and "fished salt" dissolving operations (see below). This was true where fresh lime was burned within the caustic plant, as well as where the lime sludges were reburned, the most frequent practice in the larger plants. In small caustic plants, especially those independent of an ammonia-soda operation, such as those connected with soap works, lime was commonly purchased as the slaked product. The soda ash for the causticizing operation was usually the dry product, although in some large ammonia-soda plants it was fed as a solution obtained by the steam decomposition of a slurry of "crude bicarbonate." In that case, the bicarbonate decomposition was not carried to completion and consequently, the consumption of lime per ton of caustic was somewhat higher; in usual practice, the decomposition was carried to somewhere between 80 and 86%. With either dry or "wet" soda ash in a well-regulated plant, the consumption of soda ash averaged less than 1.33 tons (as

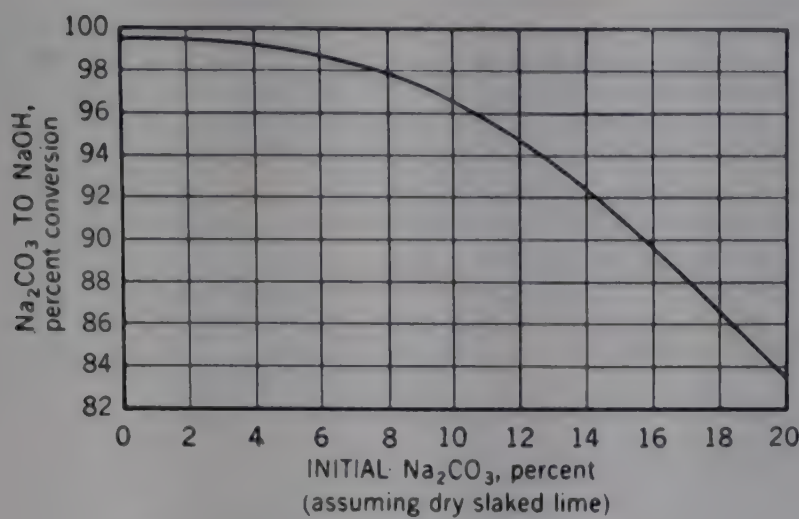


Fig. 6. Causticization equilibrium (1).

“58%”) per ton of salable “76%” caustic soda (percentages refer to Na_2O). This compares with 1.308 tons theoretically (or 1.325 with pure chemicals). About three-fourths of the loss was as alkali in the muds, and the remainder was as numerous smaller elements, generally unaccounted for.

The causticizing reaction is slightly endothermic, and a small amount of exhaust steam was used in most causticizing vessels, more to accelerate the reaction than to bring it nearer to completion. Causticizing plants were operated both batchwise and continuously, and there were two types of continuous process.

Compared to the lime process, strontium causticization (4) is favored by the extremely low solubility of strontium carbonate. At the same time, the relatively high solubility of strontium hydroxide permits causticizing to proceed up to 40–43% sodium hydroxide with relatively small settling areas and little auxiliary equipment. At 100°C , strontium hydroxide is soluble up to 21%, whereas at 10°C , its solubility is only 0.5%. In spite of these favorable relationships, the strontium process has not been studied on a plant-size scale, probably because of the relatively low availability of strontium carbonate. There is also the question of how much strontium contaminant would be tolerated by users of caustic, and how expensive its removal might be.

A few small operations using the *batch process* for the production of lime–soda caustic find local economic justification, but description is omitted since it can be inferred from the description of the two types of continuous operations.

CONTINUOUS CAUSTICIZATION PROCESSES

Continuous processes were especially applicable to large plants, and were used in the U.S.A. in capacities ranging as high as 500 and as low as 50 tons per day. The first process described (see Fig. 7) was usually called *double filtration*. Dry soda ash and dry quicklime were separately made into slurries using recycled weak caustic liquors. In a few plants, hot, incompletely decomposed sodium bicarbonate solutions and dry quicklime were fed together, but the use of separate slurries was the more normal feed to a set of causticizing tanks. These tanks were heated, generally with low-pressure steam spargers, and vigorously agitated; they were arranged in a series of three or more for minimizing short circuiting. The entire slurry or suspension from the last causticizer went to secondary causticizers. The underflow from those tanks (which acted as rough decanters) under the control of diaphragm pumps with variable stroke, was fed, together with muds from subsequent settlers, to the first of two rotary

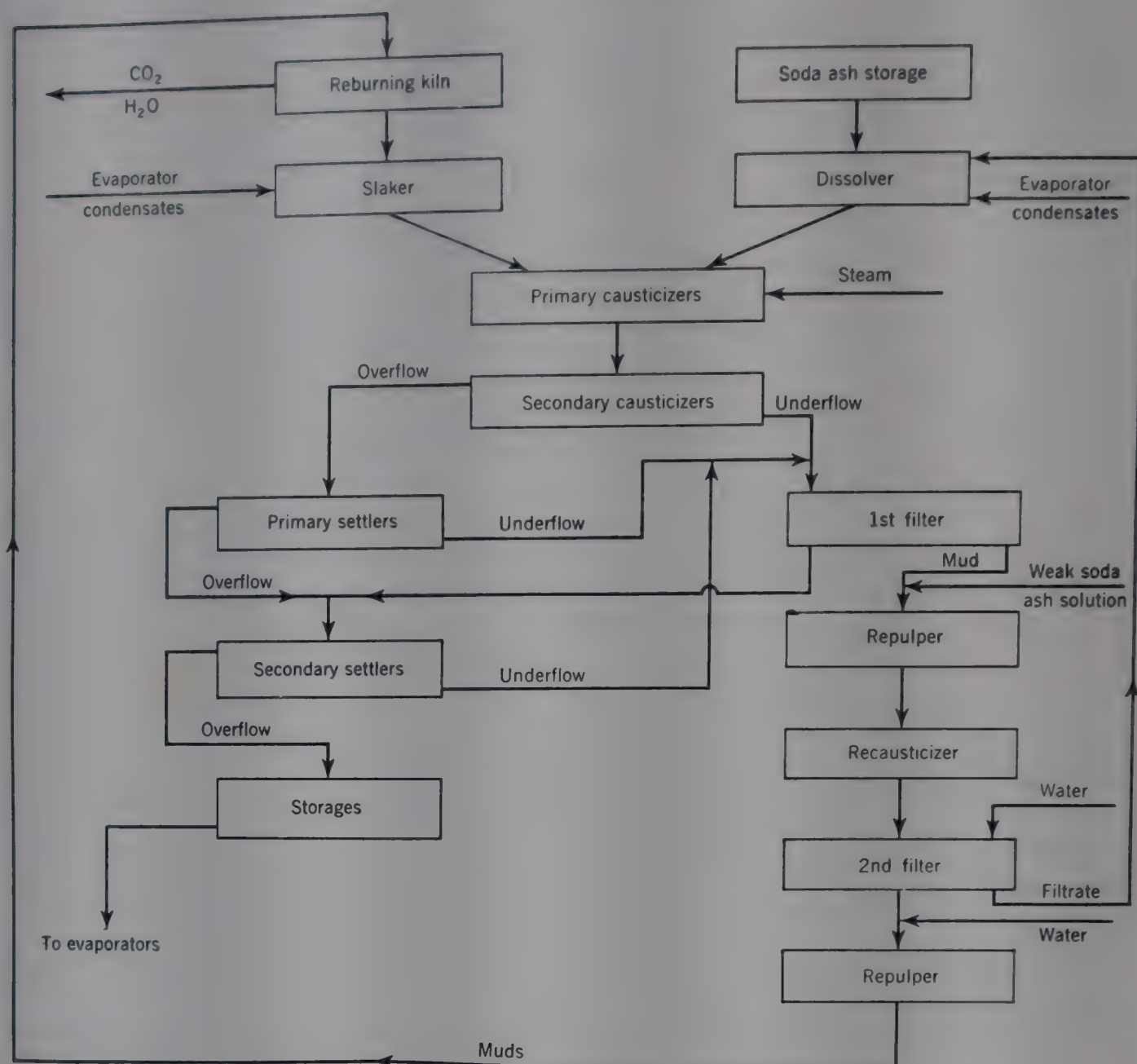


Fig. 7. Continuous causticizing with double filtration.

vacuum filters in series. The cake on the first filter was continuously washed with the second-wheel filtrate, and the first-wheel filtrate, plus the overflow from secondary causticizers, was delivered directly to a series of final settlers, from which it was delivered to 11% liquid storage. The CaCO_3 cake cut (or blown) off the first filter was repulped directly beyond the filter doctor knife with dilute soda ash solutions, normally the filtrate from the following or second filter operation. The repulper slurry was fed to the second filter basin. The cake from the second filter was repulped with alkali-free water and sent either to waste disposal ponds or to the feed storage tank for a reburning kiln of the slurry-feed type.

Another distinct type of continuous process (see Fig. 8) was usually called *counter-current washing*. In many of the countercurrent washing plants, the dissolving of soda ash, the preparation of milk of lime, and the causticizing steps were quite the same as those described for the double-filtration continuous process. From the vessel, which in the foregoing description was called a secondary causticizer but usually in the countercurrent washing plants was called the primary decanter, the underflow was delivered to a series of decantation vessels through which it flowed countercurrent to a relatively small stream of water. The overflow from the primary decanter was, as in

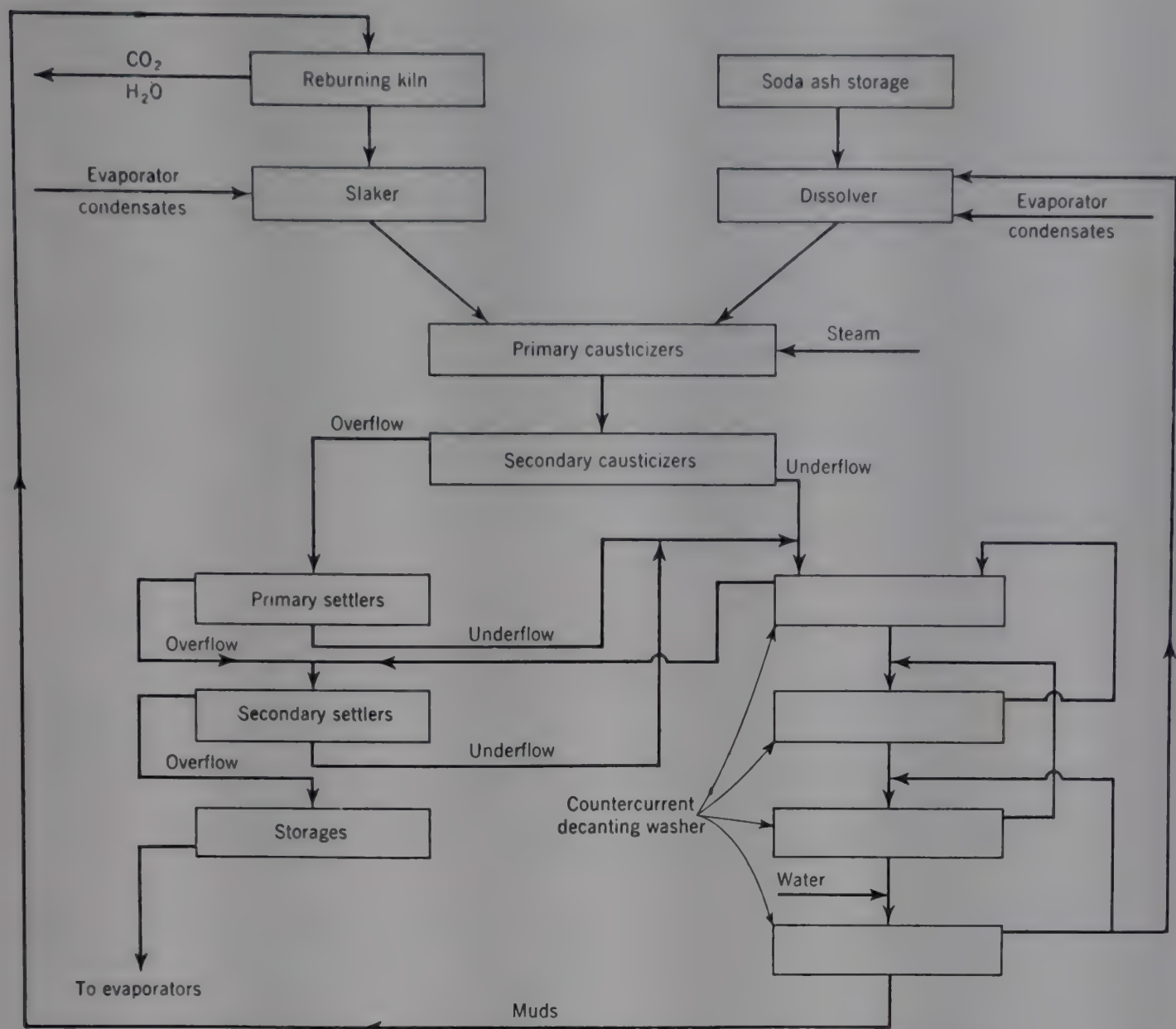


Fig. 8. Continuous causticizing with countercurrent decantation.

the other process, the raw evaporator feed. It went through primary and secondary settlers and finally to combination settling and storage tanks before being fed to the evaporators. The underflow, or mud stream, from the decanter series went either to waste beds or to reburners.

The countercurrent washing equipment often consisted of a multiple-tray washer (Dorr or Hardinge) or else multiple-tank decanters of the same general principle. The thin slurry of calcium carbonate mud in a solution of about 10% NaOH was fed to the first tank in the series, together with the almost clear overflow from the next tank in the mud series. The agitation was very mild, being actually a raking operation that concentrated the mud toward the center of each tank, from which it was removed with diaphragm-type pumps and fed to the next tank in series. Each tank in the series operated the same way. Where the tanks were superimposed, no diaphragm pumps were needed, as the muds were "lifted" by gravity, the measuring being controlled by rake speed. The overflow from the first tank in the mud series was a slightly diluted, weak caustic solution, which was added to the streams to the settlers. The water feed to the last of the washer tanks in the mud series was usually either fresh water or condensate from one of the evaporator-condensate collecting tanks. The final mud stream emerging from the last of the tanks in the mud series was pumped directly to the waste disposal stream or settling pond, or else it was

pumped to the slurry storage tanks acting as feed reservoirs for the reburning operations.

Theoretically, this process could yield a final mud stream as low in alkali as that produced with the double-filtration process, although it could not be gotten quite so dry. Therefore, in plants where the muds were reburned, it was common to place a filter right at the kiln feed floor to reduce the amount of water fed to the kiln. In this way, a dilute slurry was readily pumped to the kiln, which was usually a somewhat long distance away, and by means of the filter, the least excess of water was fed to the kiln.

Water Balance in Continuous Caustic Plants. In continuous causticizing plants there are many kinds of "water" (actually dilute alkali solutions) in circuit, and obviously a well-regulated water balance is of utmost importance to economic operation. The general principle can be laid down to conserve the caustic solution potentialities of each stream so that final muds can have the benefit of washing with the freshest water and, at the same time, minimize dilutions which tend to raise evaporation costs.

REBURNING CAUSTIC MUDS

During the years following World War II practically every large lime-soda caustic operation reburned the muds rather than quarry or purchase new limestone. The fuel consumption of a reburning kiln is of course higher than that of a limestone kiln owing to the higher water content of the muds. However, the waste disposal problem of plants without a reburner became very difficult as a result of the increased urbanization of caustic plant surroundings.

Some alkali plants incorporated cement operations and the caustic muds represented a nicely controllable calcareous input to locally available argillaceous materials. As the inroads of electrolytic caustic reduced loading of the lime-soda caustic plants, it became more and more difficult to justify the operation of reburning kilns so that in most cases these kilns were dismantled; in a few places they were converted to cement operations. The reburning operation was in most essentials the same as the operation of a "wet" type cement kiln.

Concentration of Dilute Caustic Liquors

ELECTROLYTIC LIQUORS

Caustic soda solution coming from mercury cathode electrolytic cells is very seldom concentrated because modern cells discharge the product directly at the 50% strength, which is most used in commerce. From diaphragm cells, however, a caustic solution containing 9–11% NaOH is common (see the appropriate value in Table 8, p. 696), and this contains, in addition to residual sodium chloride, some dissolved chlorine and traces of sodium chlorate. It contains substantially no solids in suspension and, therefore, requires no settling.

Because of the high salt content of dilute caustic soda solutions from diaphragm cells, the concentration of this liquor into a 50% solution suitable for commerce requires quite a different type of evaporator from that in use on lime-caustic solutions. Almost 1.3 tons of solid salt must be separated, handled and recycled, or disposed of, per ton of caustic shipped. Figure 9 illustrates a simplified flow diagram of an evaporator and desalting system which is partly triple effect and partly double effect. In many of the older evaporation plants for electrolytic caustic diaphragm liquor,

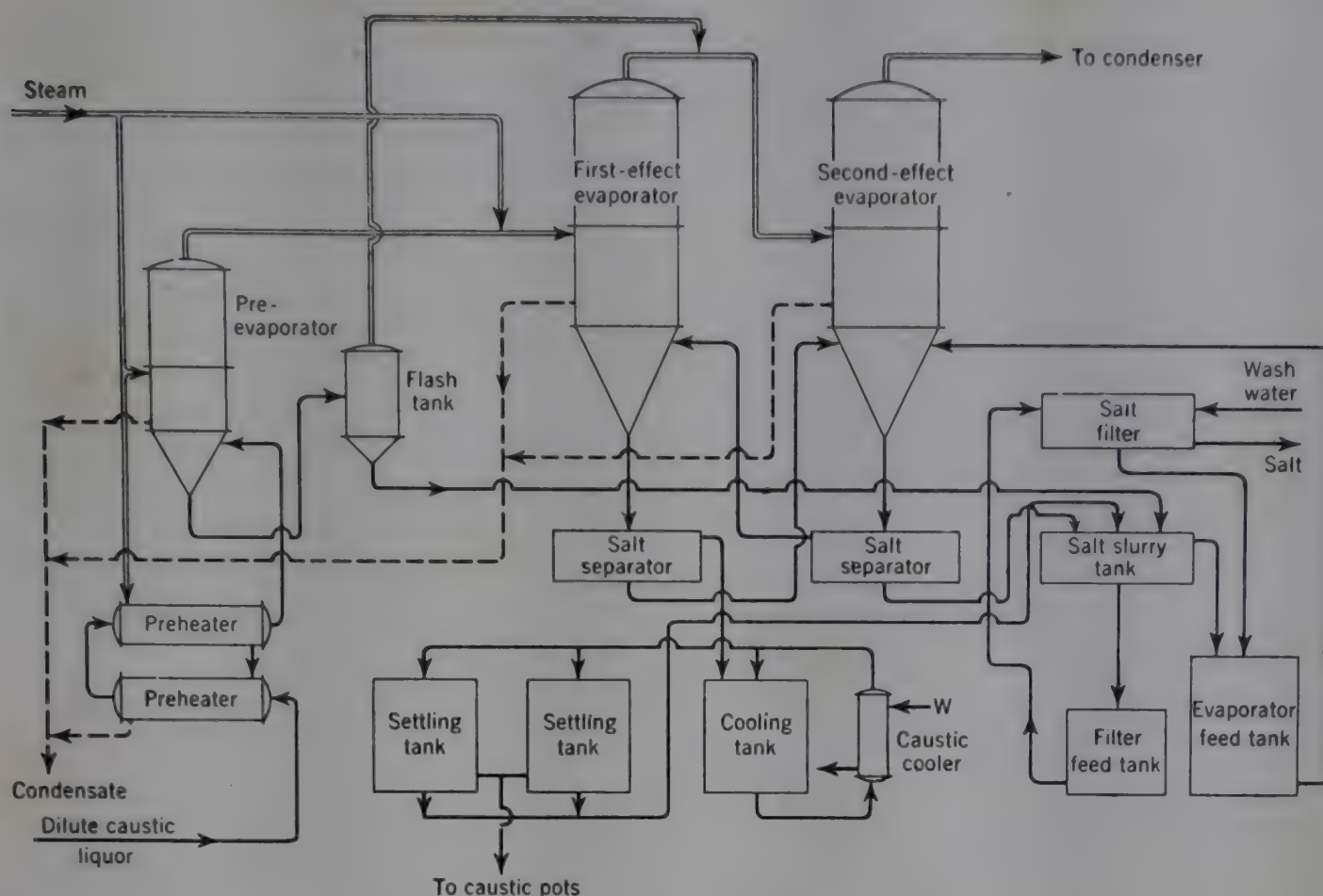


Fig. 9. Flow diagram of continuous concentration of electrolytic liquors (5).

salt was removed intermittently in contrast to the process in Figure 9. In those cases, the evaporators were equipped at the bottom of the cone, by means of appropriately valved connections, with what were known as salt boxes. Occasionally the valve was closed, the vacuum on the salt box was broken, and the heavy salt slurry was discharged to a filter or settler. Such salt was quite fine and difficult to filter, and a number of specialized designs of equipment for growing these salt crystals to a more filterable size were in use.

In the United States a 50% caustic solution is a standard tank car commodity. In European countries a 40% solution used to be fairly common, but 50% solutions directly from mercury cells have begun to predominate. The solubility of salt in 50% caustic is about 1% by weight; therefore commercial caustic made from diaphragm cell liquor by evaporation, without treatment by settling or filtration, will contain 1% by weight common salt. This amount is not objected to by many caustic users. For the rayon industry and other consumers requiring a low-salt-content caustic, lime caustic or mercury cell caustic is specified, or diaphragm caustic which has been treated for the removal of salt. During the 1960's a significant proportion of U.S. diaphragm cell caustic was treated by separating most of the salt by a counter-current liquid-liquid extraction treatment with liquid ammonia. The ammonia phase dissolves out sodium chloride and some of the chlorate. This process has the advantage that some reduction of silica and ferric oxide is possible (but unfortunately not of sodium sulfate), and it is possible to operate the process so that the salt-content is even lower than that frequently encountered with lime caustic.

The salt that is filtered from concentrating electrolytic caustic liquor is usually washed fairly free of caustic. The washing is controlled to give an optimum combination of alkali recuperation and minimum dilution. The salt is then either re-

dissolved for further feed to the cells or, as in most plants connected with ammonia-soda operations, it is added to the raw brine going to the ammonia-soda operations. Rarely, it is "finished" for sale as salt. The last two procedures have the advantage of avoiding buildup of impurities (particularly sulfates) in the cell circuit.

LIME-CAUSTIC LIQUORS

In the United States the thoroughly clarified (that is, nearly CaCO_3 free) 10–11% caustic soda solution from causticizing operations with lime is concentrated by evaporation to 50%, and the major part is shipped as 50% solution. The remainder undergoes further concentration, usually to the 70–74% insulated tank car products. An ever-decreasing minor amount is taken to the anhydrous condition. The concentration of dilute lime-caustic liquor differs from the concentration of diaphragm cell liquor in that no large amount of sodium chloride is precipitated, although a salt, commonly called "fished salt" (see below), does separate during and subsequent to the evaporation, and must be removed when making a high-quality product.

In the smaller causticizing plants, especially those with a captive market as, for example, those which used to be connected with the pulp and paper industries or soap manufacturers, the concentration was seldom taken all the way to 50%—that is, there were interdepartmental pipeline transfers of caustic soda at 25 or 35% NaOH. Such small causticizing plants are rapidly disappearing under the competition of the low incremental costs of the large alkali factories.

The concentration to 50% is usually conducted in a multiple-effect evaporator. Some of the older large plants still use a combination of equipment—one evaporator taking the solution to 24 or 26% NaOH and another to 50%—but this practice is relatively obsolete and stems from the time when it was widely considered inadvisable to operate caustic evaporators with a steam pressure much greater than 10 or 15 psig.

Caustic made from fresh lime (in plants without lime sludge reburning kilns and even in those plants that reburn lime with fuel having a high sulfur content) contains a considerable amount of SO_4^{2-} ion, as well as the excess sodium carbonate. The solubility of sodium sulfate and sodium carbonate in the 11% caustic is considerably greater than in the 50% caustic, and consequently these solids precipitate during the evaporation. This "fished salt" has a composition that is not constant and is generally about half as rich in sodium sulfate as is burkeite, $2\text{Na}_2\text{SO}_4 \cdot \text{Na}_2\text{CO}_3$. Supersaturation of these solutions during cooling is variable and troublesome. A fished salt composition which tends to come out of solution quicker and to settle out a little more readily is usually sought. For that reason it is often found, in causticizing plants, that sodium sulfate will be added from time to time in order to maintain a desired "sulfate-to-carbonate" ratio. Generally this is done by adding fished salt to the system before the causticizer; fished salt is stored in relatively small quantity for the purpose. In natural gas-fired reburner plants having efficient lime recycle such that the input of SO_4^{2-} ions is very small, satisfactory precipitation and separation of sodium carbonate can be obtained by itself (6).

In the usual evaporating plant the fished salt begins to crystallize out (at the temperatures within normal evaporators) at about 22–24% NaOH. In a regular parallel-flow, triple-effect evaporator, which takes the liquor from the 10–11% causticizer product right up to a product suitable for making 50% liquor for shipment, this critical 22–24% concentration is reached only in the third effect. For that reason, the third effect was invariably operated with a relatively large body of liquor so that

the fished salt crystals could grow to reasonable size within the evaporator, thus avoiding rapid fouling of the heat-transfer surfaces. In quadruple-effect evaporators, and even in improperly managed triples, some of the fished salts tended to precipitate in the intermediate bodies and troublesome fouling of the heat-transfer surfaces was experienced. Fished salt was usually removed by continuous cooling and decantation. The underflow, from decanters, was treated by thickening, and in some cases, filtration, with recycle to the causticizers.

As the concentration operation of lime caustic was at one time a big consumer of steam and required very expensive evaporator equipment, there were many competing multiple-effect designs with complex countercurrent and parallel-flow hookups. Many years ago most of these evaporators were made of steel and iron and in a few cases were equipped with copper tubes. However, as the purity demands of the rayon industry became more difficult to meet, evaporator equipment was largely made with nickel surfaces wherever there was liquid contact. During the early 1960's, in the United States at least, lime process causticizing plants were being shut down except under relatively isolated conditions.

Clarification of Evaporated Lime-Caustic Liquor. The solubility of fished salt in caustic liquor at about 50% NaOH is not well delineated, perhaps because the approach to equilibrium is extremely slow, and perhaps also because there are many solid phase possibilities among the ions present. The solubilities are lower at low temperatures than at the moderately high temperature of the evaporator (about 100–140°C). For this reason, it was necessary to have fairly extensive clarification equipment in caustic evaporating plants. This usually consisted of holding tanks, equipped with cooling coils, together with quite extensive settling tanks and, in some cases, final filters. Caustic liquor that is close to equilibrium with fished salt at 30°C is satisfactorily low in sulfate and carbonate ions. However, in practice this equilibrium could not often be reached before it was necessary to ship the product; consequently, the solution became slightly cloudy on its way to or in storage at the customer's works. Hence, the so-called "polished liquor" was made by cooling to temperatures below any anticipated on its way to the customer, and agitating, ageing, and filtering at a temperature somewhat below the usual room temperature.

STORAGE AND SHIPMENT OF CAUSTIC LIQUORS

In all caustic soda plants, especially lime-caustic plants, it is difficult to accelerate or decelerate operations to follow minor variations in shipping schedules because of the large number of sedimentation and decantation vessels in both weak- and strong-liquor circuits. The underflow and overflow streams invariably get out of their somewhat delicate balance whenever there is a rate change. Thus it is common in large modern caustic plants to have fairly extensive storage facilities for the product. These storages do not differ in any essential respect from normal storages for such a high-density liquid product. In modern practice, it is of course important to minimize or eliminate iron contamination, and for this reason the tanks are either nickelclad, or, more frequently, coated with a specially devised caustic-resistant paint, usually with a rubber, epoxy, or ethyl cellulose base. In addition to the antifouling feature, caustic storages also require special provisions for occasional removal of the very slowly accumulating last traces of settled solid impurities. The product, therefore, is not taken off from the very bottom of the tank, but a small distance above, and means are provided on tanks for occasionally washing out the sludges.

Shipment of 50% caustic soda is usually made in tank cars, tank trucks, or tank barges. The most common sizes of cars are 8,000 and 10,000 gal, representing about 26 and 32 tons, respectively, of equivalent NaOH. Most caustic manufacturers own fleets of tank cars, but in the United States there are also a number of tank-car-operating companies leasing cars to alkali manufacturers. The tanks for high-quality caustic have to be protected in the same manner as the storage tanks to minimize iron contamination. Nickelclad vessels for caustic soda liquor storage and shipment are in use, but at 50% NaOH and moderate temperatures their cost has less justification than at higher temperatures and concentrations.

Caustic soda at 50% concentration becomes extremely viscous and even freezes (or sludges) at winter temperatures; hence the tank cars must be equipped to meet this situation. It was formerly common practice for all 50% NaOH tank cars to contain steam coils which the customer connected a few hours before unloading. There was some hazard in the operation of these coils. A broken coil might drain the car dangerously at a time when it was being connected up for steam. Also, it is hard to maintain a good coating of a resistant paint on the iron surface at the temperature of a steam coil. In modern practice steam coils are welded to the outside of the tank and approximately 6 in. of insulation is applied over the tank and coil. The insulation is protected with a thin metal jacket. Externally coiled cars provide flexibility of service for both 50 and 70% liquor. Noncoiled cars are limited to 50% liquor and warm climates. Before loading, caustic cars are thoroughly washed out with hot water and the lining and all safety parts are meticulously inspected. Caustic tank cars are usually filled by weight on track scales.

CONCENTRATION BEYOND 50%

In the U.S.A. an increasing amount of caustic soda is reaching the market as 70 to 74% hot solutions in heavily insulated tank cars, and a steadily decreasing amount is reaching the market in the anhydrous form in 700-lb drums. Formerly, a very large part of the product was shipped in the anhydrous condition, because tank cars had not yet been sufficiently developed for its shipment, and because consumers large enough to use tank car lots were relatively few. Today (1962) the anhydrous product is used mostly in flake form for special purposes and the fused solid anhydrous is used principally for the export market. The 70 to 74% solution, usually called "high-concentrated liquor," is prepared in steam-heated, single-effect, nickel evaporators, and the portion of the product that is not shipped as such is used as feed for the anhydrous operation. Some caustic plants do not make a 70 to 74% product for shipment, but feed the 50% or 40% solution directly into the equipment for making the anhydrous product.

High-Concentrated Liquor (70–74%). Production of high-concentrated liquor is a relatively simple operation. The raw material is the clarified salable 50% caustic liquor, and it is usually evaporated in single-effect, moderate-pressure, natural-circulation evaporators. A nickel heating surface is required, both for reasonable life and to avoid iron contamination.

Iron is dissolved fairly rapidly in hot 70% caustic solution; even nickel goes into solution more rapidly than is desirable for a high-quality product so that some evaporators are electrolytically protected to inhibit nickel contamination. Control of the operation is usually on the basis of specific gravity and temperature of the discharging stream. Feed liquor and steam pressure are regulated to control the desired pro-

duction rate. No additional “fished salt” precipitates out during concentration; hence the product from the evaporator is ready for shipment directly, and is stored and loaded in much the same way as 50% caustic liquor.

Anhydrous Caustic. The molten anhydrous caustic is allowed to solidify in single-trip steel drums of about 700-lb capacity. Anhydrous caustic is also marketed in the form of flake and granular material, either to ease the problem of dissolving or for purposes of dry blending with other materials. In these forms the anhydrous caustic is shipped in various sizes of steel drums, and to some extent, in polyethylene-lined, multiwalled paper bags.

Until about 1950, anhydrous caustic was produced by evaporating 50% or 73% caustic solution in direct-fired, cast-iron pots. To minimize attendance and maintenance costs, the pot process has been largely superseded.

Anhydrous caustic production facilities installed since 1950 employed various modifications of tubular, flash-type evaporators using high-temperature heating media. The earlier of these installations used Dowtherm vapor condensing in the flash evaporator heating chest. The more recent installations have used either Dowtherm completely in the liquid phase or molten salt. Materials of construction in contact with caustic are low-carbon nickel, or Inconel. Corrosion becomes a serious factor when the caustic solution fed to the evaporator contains chlorate or dissolved oxygen. Therefore, it has been common practice to treat the caustic solution for removal of oxygen and chlorates before feeding to the evaporator.

In order to obtain a product containing less than 0.5% water, temperatures in the range of 380°C are required. These temperatures can be attained more easily with molten salt than with Dowtherm (either liquid or vapor) because decomposition of Dowtherm is significant at temperatures only slightly higher. The molten salt generally used is a eutectic mixture of potassium nitrate, sodium nitrite, and sodium nitrate.

High-Quality Caustic Soda

The consumers of caustic soda, in common with most other chemical consumers, continually become more exacting in their demands for superior product quality. Table 1, which gives the trends in uses of caustic soda, shows the fastest growth rates in those fields where high purity is of comparatively great and increasing importance.

Table 1. Uses of Caustic Soda in U.S.A.
(thousands of 2,000-lb tons)

	1930		1940		1950		1960	
	Tons	%	Tons	%	Tons	%	Tons	%
soaps and detergents	100	15.3	103	9.2	145	5.8	105	2.1
chemicals	100	15.3	212	19.0	850	33.8	2,150	43.3
petroleum refining	117	18.0	105	9.4	200	8.0	250	5.0
rayon and cellophane	110	16.9	230	20.6	525	20.9	555	11.2
lyes and cleansers	22	3.4	48	4.3	125	5.0	170	3.4
textiles	63	9.7	48	4.3	140	5.6	250	5.0
pulp and paper	10	1.5	78	7.0	185	7.4	480	9.7
exports	42	6.4	105	9.4	130	5.2	238	4.8
miscellaneous	88	13.5	189	16.8	210	8.3	774	15.5
total	652	100.0	1,118	100.0	2,510	100.0	4,972	100.0

The viscose industries were the first to insist not only on previously unheard of low-impurity concentrations, but also on constant levels of low-impurity content within narrow tolerances, because of difficulty in xanthating and spinning operations. The industries such as petroleum refining, pulp and paper, dyes and cleansers, where consistently high quality is not of such great importance are, as a group, consuming smaller and smaller fractions of the caustic soda market.

The first high-purity U.S.A. caustic, the so-called Castner mercury cell product from Niagara Falls, practically cornered the viscose market in the early years of rayon production following World War I. To meet that competition, but more because of the then rapidly expanding demand for viscose-grade caustic, the lime-caustic makers, and later the diaphragm cell operators, devised and developed methods for making purer product, and for a time marketed it as special grades at premium prices.

There are two general methods of producing pure caustic: the first is to separate out the impurities; the second is to manufacture with meticulous care to avoid all input of impurities. Early efforts to crystallize caustic from its mother liquor belong in the first category, and so does the widely used method of purifying diaphragm cell liquor with liquid ammonia. On the other hand, the production of mercury cell liquor and the special qualities of lime caustic belong in the second category.

In an ordinary lime-causticizing plant including a reburning cycle, the "lime body" can be kept substantially constant and the lime makeup required will be extremely small. Under these conditions, the lime body gradually purges itself and becomes extremely pure. From then on, the production of high-quality caustic involves only using a fuel in reburning that does not contaminate the lime, and meticulous care at every point to avoid input of any objectionable contaminant. This is done by using nickel apparatus in the caustic circuits, high-quality brick in the reburning kilns, and ashfree gas or oil fuel.

The results of the efforts of lime-caustic manufacturers are evident in the first three or four columns in Table 2, which show a marked reduction in the "earth" impurities.

With the lime process substantially replaced, the problem of high-purity caustic has become one of thorough brine purification for both the electrolytic processes, and salt and chlorate removal from the concentrated diaphragm cell liquor. The mercury cell operation requires superior water quality in the denuder cell.

The purest caustic has always come from mercury cathode electrolytic cells, and, in the light of recent advances in the use of these cells, the availability of this super-product will not only continue but will increase. The critical nature of the low tolerances for heavy-metal or trace impurities has demanded new techniques in resaturated anolyte treatment; in the use of better anode materials; in the use of completely demineralized water at the denuders; and in surgical cleanliness in all handling, storage, and shipping.

Prices and Uses

Tables 1 and 3 give some history and details of the uses of caustic soda over the thirty-year period ending in 1960. The uses have become increasingly diversified, especially in the field of chemicals. The traditional uses in the fields of soap, textiles, and petroleum refining, although still substantial, show percentage decreases. In highly industrialized countries, the mid-century decades have witnessed aggressive

Table 2. Analyses of U.S.A. Commercial Caustic Soda Reaching Market

Constituents ^a	Lime process, 50% liquor					1960			Anhydrous from diaphragm cells ^c
	1920	1930	1940	1950	1960	Diaphragm cells, 50% liquor		Rayon grade, mercury cells	
						Regular	Treated		
% by wt (lb/100 lb soln)									
NaOH	47.	49.	50.	50.	50.	50.	50.	50.	97.6
Na ₂ O	36.3	38.	38.8	38.8	38.8	38.0	38.9	39.0	76.2
Na ₂ CO ₃	0.12	0.12	0.10	0.15	0.15	0.14	0.12	0.03	1.0
NaCl	0.28	0.25	0.14	0.30	0.30	1.10	0.10	0.01	1.3
Na ₂ SO ₄	0.12	0.10	0.04	0.07	0.07	0.03	0.02	0.002	0.15
SiO ₂	0.20	0.15	0.02	0.02	0.02	0.024	0.011	0.002	0.028
Al ₂ O ₃	{ 0.015 ^b	{ 0.014 ^b	0.003	0.007	0.004	0.0015	0.0015	0.0011	0.002
Fe ₂ O ₃			0.008	0.0004	0.0007	0.0010	0.0005	0.0003	0.0025
CaO	{ 0.007	{ 0.006	0.002	0.001	0.001	0.0035	0.0030	0.0015	0.005
MgO			0.001	0.001	0.001	0.0020	0.0015	0.0010	0.003
Parts per million									
Mn			0.4	0.8	0.8	0.4	0.4	0.4	1.0
Cu			0.4	0.1	0.1	0.8	0.8	0.7	1.5
Pb				0.5	0.5	0.5	0.5	0.5	0.5
Ni		0.1		1.0	1.0	0.8	0.8	0.5	3.0
Sr				10.0	10.0	25.0	25.0	9.0	20.0
NaClO ₃				100.	150.	1,000.	9.0	4.0	<1.0

^a Ag, Hg, and As₂O₃ are also frequently determined by spectrographic and other methods, but the concentrations are usually lower than the differences between methods of analysis, as yet not standardized.

^b During the 1920's and 1930's only R₂O₃ was determined.

Table 3. Recent U.S.A. Chemical Uses of Caustic Soda (7)

Use	Thousands of 2,000-lb tons		Percentage of market	
	1954	1958	1954	1958
intermediate coal tar products	91	132	8.1	8.1
organic chemicals	489	890	43.8	54.2
inorganic chemicals	294	321	26.3	19.6
plastics	140	158	12.6	9.6
captive uses	103	139	9.2	8.5
total	1,117	1,640	100.0	100.0

activity in finding new uses for caustic soda, in order to minimize the chlorine-caustic soda demand imbalance. In the unindustrialized countries, the same incentive has required even more intensive activity for finding new uses for chlorine. The results of the sales pressures in the United States are evident in Table 3. Figure 10 shows the price history of caustic soda in the United States.

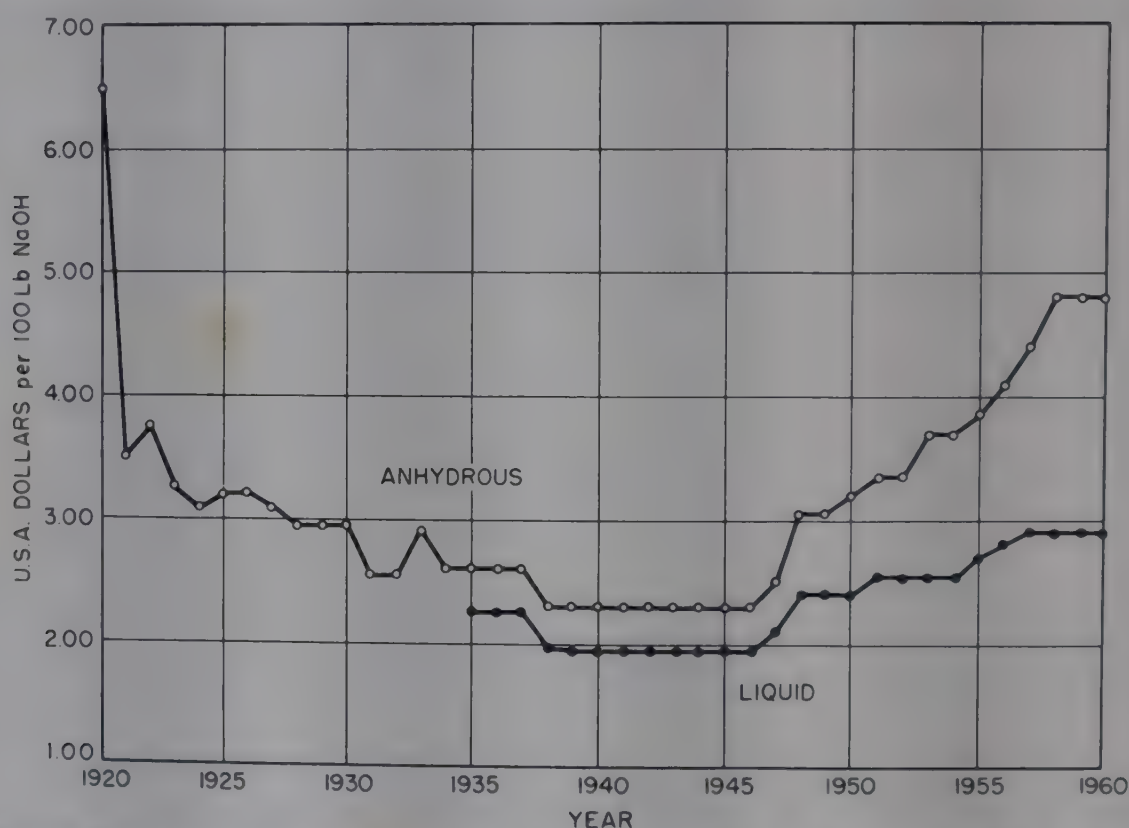


Fig. 10. United States price history of caustic soda. Prices for the anhydrous are for 76% Na_2O in 700-lb drums in carload lots at works; for the liquid, 50% NaOH in the seller's tanks.

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ALKALI METALS. See Cesium; Lithium; Potassium; Rubidium; Sodium.

ALKALINE EARTH METALS. See Barium; Calcium; Strontium.

ALKALOIDS

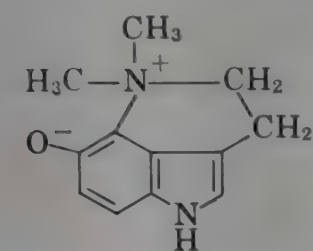
The first section of this article gives examples of the almost limitless variety of heterocyclic systems with special emphasis placed on those alkaloids which are of importance or interest because of their physiological properties. The second section describes the principal methods for commercial extraction of alkaloids. For a more detailed account of the uses of certain alkaloids, see also articles such as Analgesics and antipyretics; Cardiovascular agents; Insecticides; Protozoal infections, chemotherapy; Psychopharmacological agents. See also Heterocyclic compounds.

Alkaloids, survey.....	758
Bibliography.....	777
Alkaloids, history, preparation, and use.....	778
General references.....	809

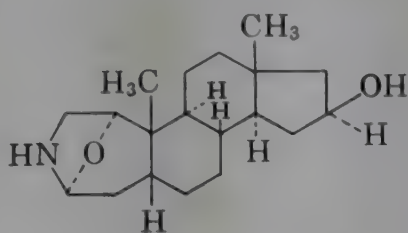
SURVEY

Almost a century and a half ago Sertürner isolated morphine from opium. Although he was not the first man to isolate this substance, he did recognize it to be a representative of a new class of substances, "the vegetable alkalies." Meisner in 1818

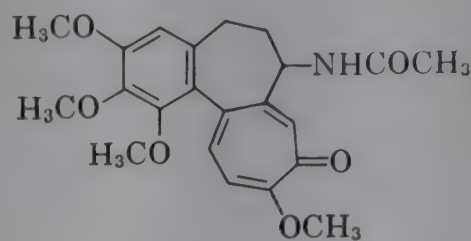
proposed that such vegetable alkalies should be called "alkaloids." Today the term alkaloid is generally used to denote a basic, physiologically active, nitrogen heterocycle of fair complexity which is obtained from plant sources. However, this definition, rigidly applied, would result in the exclusion from standard treatises of simple primary amines such as the cactus hallucinogen, mescaline (45). Other exceptions to the rule are novel bases of animal origin, for example dehydrobufotenine (1) from the toad, and samandarine (2), a secretory product of the salamander (1,2). Certain new basic carbocyclics of natural occurrence are still included in books on alkaloids because at one time they were thought to be nitrogen heterocycles. The mitotic poison, colchicine (3), from the autumn crocus represents one case and the nitrophenanthrene, aristolochic acid (62), represents another.



dehydrobufotenine (1)



samandarine (2)



colchicine (3)

Occurrence

Up to the end of 1957 the isolation of some 2233 alkaloids was recorded. These alkaloids are found in 3671 plants belonging to 156 families. This represents less than 5% of all species. Alkaloids are found to occur mainly in the flowering plants and principally in the dicotyledons rather than the monocotyledons. Several very interesting alkaloids, however, are recorded from lower plants. The rye fungus, *Claviceps purpurea*, produces among other compounds, ergotamine (8); the club mosses, *Lycopodium*, make ananoline (14); and horse-tails, *Equisetum*, manufacture the peculiar bicyclic, palustrine (15) (3). Alkaloids if they occur at all in the *Gymnospermae* (eg, *Pinus*, *Ephedraceae*) have so far turned out to be derivatives of pyridine or β -phenylethylamine. Alkaloids may occur in all parts of the plant, although in different families alkaloids do appear to be concentrated in specific locations such as the bark, roots, seeds, or leaves. Alkaloids may be further complicated and exist as glycosides (solanum) or polyesters (senecio, veratrum, aconite) and in the extreme case the alkaloid is a simple amine, such as ethanolamine, esterified with a complicated carbocyclic, such as a diterpene acid. Cassaine (106) is an example of this last case.

Isolation

Alkaloids in plant extracts are usually detected by making use of their ability to form water-insoluble salts with suitable anions. Reagents used for this purpose are mercuric iodide in aqueous potassium iodide (Mayer), phosphomolybdic acid (Sonnenschein), bismuth potassium iodide (Dragendorff), and, occasionally, picric acid. Advantage is usually taken of the basic character of an alkaloid in the isolation procedure. An extraction of the plant is generally carried out so that the end result is an aqueous acidic solution. This can be extracted with solvents to remove nonbasic substances. Then the alkaloids, liberated by the addition of an appropriate inorganic base, are brought into a suitable solvent, which is dried, and concentrated to dryness.

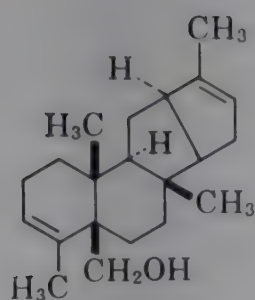
This general method cannot be applied to either quaternary bases (curare) or to most *N*-oxides (senecio); the former are isolated by preparing a water-insoluble salt such as picrate or reineckate, and with the latter the problem can be simplified by reduction to the tertiary base. Advantage is taken of any special properties—for example, weak base acetates and hydrochlorides are generally extractable into chloroform or methylene chloride, the stronger base salts remaining in the aqueous medium. The most difficult part of isolation work is not the preparation of crude alkaloids but the separation of the components of the mixture. In the last twenty years, important new techniques have been developed for the analysis of such mixtures and their practical separation. Thus paper and gas chromatography can reveal much about the nature and number of the alkaloids present. Column and partition chromatography as well as countercurrent distribution are extensively used to obtain excellent separations in complex mixtures. Contrary to earlier results it is now recognized that an alkaloid-producing plant elaborates a large number of bases (eg, curare (4), rauwolfia (5)) although only a few may be present in any substantial quantity. Also we know that the chemist occasionally produces artifacts during the isolation procedure, for example, via autoxidation (6) (tabernanthe) or isomerization (7) (hunteria).

Structure and Classification

In the classical period an alkaloid could only be characterized via its melting point, optical rotation, salts, and other functional derivatives. In order to establish the presence of a functional group, a derivative had to be prepared. The use of color reactions to detect different structural moieties became a highly developed art, and a skilled investigator could often draw surprisingly accurate conclusions. These techniques have been largely superseded by modern recording ultraviolet and infrared spectrophotometers from which a wealth of structural information can be derived. The recent introduction of reliable proton magnetic resonance recorders provides another new way of looking at molecules; in this case the proton topography is deduced and many details of structure are obtained, which could not be ascertained in any other way. The exact molecular weight of the compound, if volatile enough, may be determined by mass spectrometry and if its breakdown pattern is characteristic enough, a complete structure may be obtained. So far, the only physical technique described in which the alkaloid is not recoverable is the last and here only 150 γ need be used. X-ray diffraction can be used to characterize single crystals or powders. Ever since the discovery by Bragg that x-ray diffraction by crystals could be used to solve structures, it has been recognized that, in principle, chemical methods of degradation had been rendered superfluous. However, until recently, the calculations involved have been so time consuming and tedious that few organic compounds had been examined. The advent of computers has changed all this and from the diffraction patterns of a single suitable crystal of an alkaloid hydriodide, the complete stereo structure can be calculated. In favorable cases this takes less than six months.

A good example of a structure determined by this method is telepogine (4) from the grass, *Telepogon elegans*, a representative of a hitherto unknown class of diterpenoid alkaloids upon which no chemical work had been carried out (8).

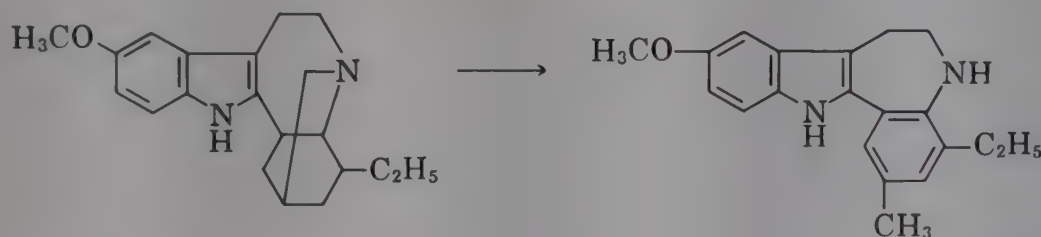
With the knowledge available from classical chemistry and the information provided by physical methods, many structural problems can be reduced to either a partial synthesis or degradation. The challenge which now faces the chemist is no



telepogine (4)

longer degradation but efficient rapid stereospecific synthesis. An outstanding example is the total synthesis of commercially important reserpine (**93**), which can be carried out at a price competitive with the cost of its isolation from *Rauwolfia vomitoria*.

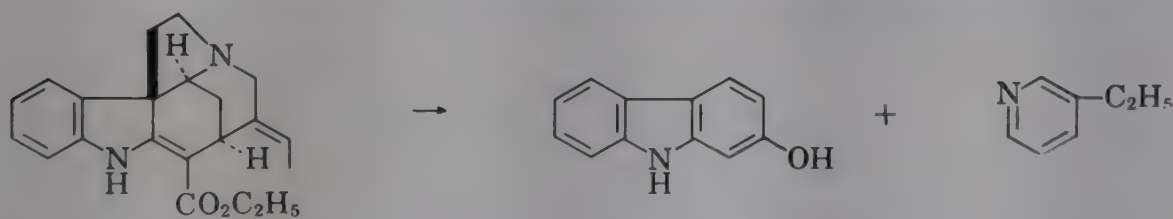
There is no single method of degrading an alkaloid because alkaloids are so widely diversified in type. For many simple compounds, operations on the basic nitrogen (Hofmann, von Braun, Emde degradations) are carried out. In highly condensed heterocycles, these methods are often unsatisfactory or do not lead to useful derivatives. Therefore, other functional groups are modified. Dehydrogenation (selenium, sulfur, palladium, zinc) and potash fusion have been used to obtain aromatic compounds containing all or part of the original carbon, nitrogen, and oxygen atoms, linked as they were in the hydroaromatic molecule. The pentacyclic alkaloid, ibogaine (**5**), upon selenium dehydrogenation (9) yields (**6**). Here only one bond of the original base has been broken.



ibogaine (5)

(6)

It should be noted that under the correct conditions a complicated heterocycle may split up into simple compounds as does akuammicine (**7**) in methanol at 140°C (10).



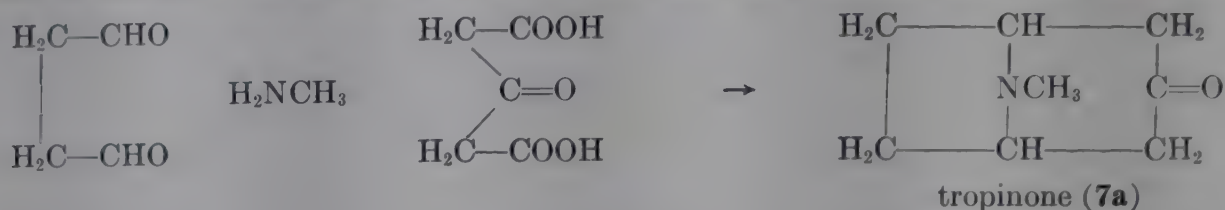
akuammicine (7)

The pace of modern research is well illustrated in the history of reserpine (**93**). It was discovered in 1952, its structure was elucidated in 1955, and a commercial synthesis was a reality in 1956.

Function and Origin of Alkaloids

The function, if any, of alkaloids in plants is not known. The alkaloidal content of plants depends on many variables, such as age, geographical location, and climatic conditions. There are cases of a plant yielding no bases in spite of its being morphologically indistinguishable from an alkaloid-containing variety. Little is known about

the intimate details of alkaloid biosynthesis although the nature of some of the enzymatic operations is now understood. These all have their equivalents in the normal practice of chemistry. The most important of these steps—the one which sets up the heterocyclic structures—is one, or more, Mannich, Pictet-Spengler, or phenol-phenol oxidative coupling reactions with suitably activated systems. Many alkaloids have been synthesized in the laboratory using such reactions under conditions (pH \sim 7 in water) thought to mimic the natural process. The first and most famous example is the synthesis in 1917 of tropinone (**7a**) by a double Mannich condensation.



Many more examples have been recorded in the last forty years, as progress is dependent on the development of methods for synthesizing the required aldehydes. Amino acids, the obvious biochemical precursors of aldehydes, have been the favorite postulated source of alkaloids. Recent studies of alkaloid biosynthesis using compounds labeled with ^{14}C have provided confirmation for some of these ideas, but other long-accepted notions have had to be discarded. For example, the origin of the pyridine ring in nicotine is still not known; it apparently does not come from anthranilic acid as has been demonstrated in the case of microorganisms. Also the D/E ring of the pentacyclic indole alkaloids (eg, yohimbine (**84**)) is not formed from tyrosine or its equivalent as had been believed and may have an acetate and malonate origin (11). Only in the case of some benzyloquinoline alkaloids and morphine has any progress been made toward an understanding of the discrete stages of the biosynthetic reactions. The major contribution of the organic chemist to the above problems has been, and still is, the isolation and determination of the structure and stereochemistry of as many alkaloids as can be done, since this can reveal certain recurring patterns and common denominators. Thus it has become clear that the larger number of indole alkaloids must originate from a common intermediate (**89**) and that the carbons equivalent to the starred atom of yohimbine (**84**) all have the same absolute stereochemistry. This last fact must be of the utmost biochemical significance.

Classification of Alkaloids

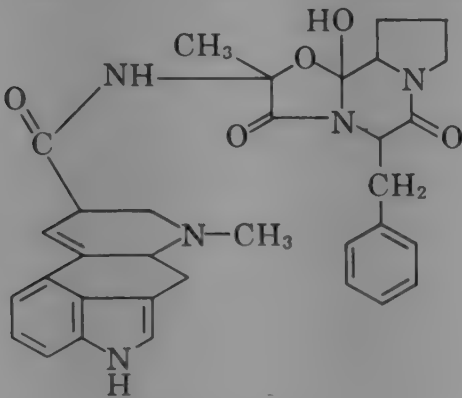
The name of an alkaloid usually provides a clue to its botanical source. This convention is particularly useful when the structure of the base is not known. For some classes of alkaloids the botanical genus, or even family name, can be used to describe a particular type of heterocyclic system or systems. Thus the term cinchona alkaloid means a particular tetracyclic moiety whereas opium alkaloid refers to any one of a number of different bases isolated from the opium poppy. When the botanical source of important alkaloids is obscure, the alkaloids have often been given names indicative of their source. Thus the curare alkaloids are divided into three types, para (tube or bamboo), pot, and calabash (or gourd) curares. For the purposes of this article more emphasis is placed on representative alkaloid types and their interrelationships rather than on descriptions of all the alkaloids from individual plants.

Alkaloids from Fungi. Morphological complexity of a plant is not necessarily reflected in the alkaloids which it produces. Among the lower plants, ergot (*Claviceps*

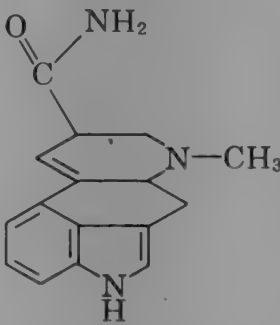
purpurea) produces six interconvertible pairs ($\beta\gamma = \alpha\beta$ unsaturated esters) of alkaloids of considerable complexity. The most important of these is ergotamine (8), useful for its oxytocic effect on the uterine muscle. Such a combination of a complicated heterocycle (in this case lysergic acid) with a peptide moiety is common in fungi but rare in higher plants. The pronounced central nervous activity of synthetic lysergic acid amides has been known for many years and it is interesting to note that it has been shown that lysergic acid amide (9) is the active hallucinogen of the convolvulaceous plants, *Ipomea tricolor* and *Rivea corymbosa* (12). These plants have had a long history of use by Mexican Indians in primitive religious ceremonies. Investigations of other fungi known to be used for their central nervous effects have shown that alkaloids are the active agents. *Psilocybe mexicana* elaborates the unusual indole phosphate, psilocybine (10) (13), and fly agaric (*Amanita muscaria*) has the quaternary, muscarine (11). Table 1 shows the structures of some of the alkaloids from lower plants.

Lycopodium Alkaloids. The club mosses (lycopodium) have a group of complex bases which have no parallel in higher plants. Representative examples are anofoline (12) (14), lycodine (13) (15), and annotinine (14) (16). See Table 1.

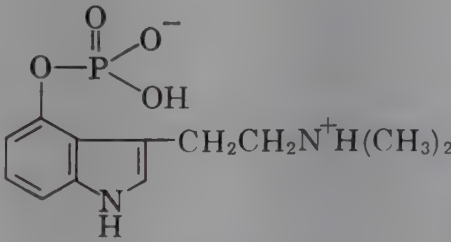
Table 1. Alkaloids from Lower Plants



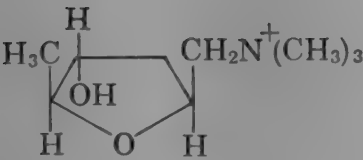
ergotamine (8)



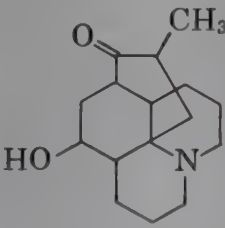
lysergic acid amide (9)



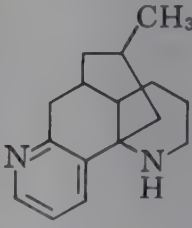
psilocybine (10)



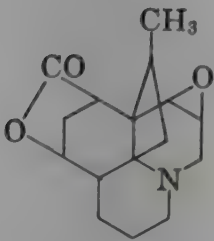
muscarine (11)



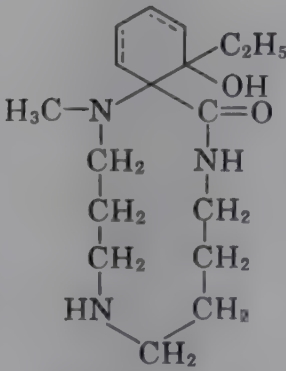
annofoline (12)



lycodine (13)

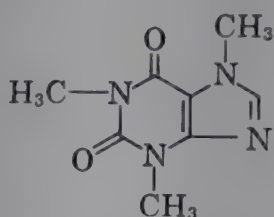


annotinine (14)

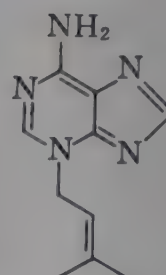


palustrine (15)

Purine Alkaloids. Just as primitive peoples discovered the hallucinogenic effects of the fungi so did they also discover other plants whose aqueous extracts made very satisfying beverages. Some of these plant products, coffee and cacao beans, kola nuts, and tea leaves, are of great commercial and social importance. The principal active component is the purine, caffeine (16), which occurs up to 1% in coffee beans, 3% in kola, and 4% in tea. The lower methyl derivatives, theobromine and theophylline, as well as other purines, are also found but are not so important physiologically. Like the amides referred to earlier, the purines are virtually nonbasic. Therefore, they do not meet the general definition of an alkaloid, and in spite of their physiological activity are no longer discussed in modern alkaloid texts. Some two million pounds of synthetic caffeine are used in commerce each year, mostly in bottled beverages. From the *Leguminosae*, the honey locust (*Gleditsia triacanthos*) yields the purine, triacanthine (17), which because of its isopentyl side chain can also be regarded as a hemiterpenoid alkaloid (17).



caffeine (16)



triacanthine (17)

Pyrrolidine Alkaloids. Very simple heterocycles are known. Pyrrolidine is found among the minor alkaloids of tobacco along with its *N*-methyl derivative and *N*-methylpyrroline. β -Methylpyrrolidine is a constituent of black pepper. From *Stachys tubrifera* and lucerne hay the quaternary, stachydrine (18) (proline betaine), has been isolated. Hygrine (19) and cuskohygrine (20) have both been obtained from Peruvian coca leaves. Table 2 shows the structures of these alkaloids.

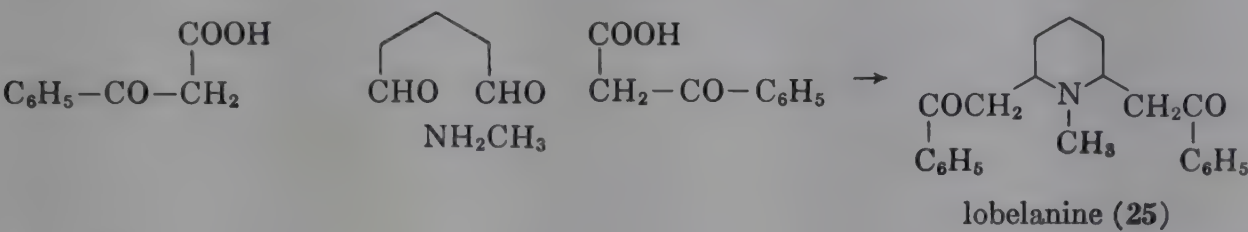
Table 2. Pyrrolidine and Piperidine Alkaloids

<p>stachydrine (18)</p>	<p>hygrine (19)</p>	<p>cuskohygrine (20)</p>
<p>piperine (21)</p>	<p>ricinine (22)</p>	<p>trigonelline (23)</p>
<p>arecoline (24)</p>	<p>nicotine (26)</p>	<p>anabasine (27)</p>

Piperidine Alkaloids. In the pyridine series, methylpyridines, 3-methoxy-pyridine, pyridine itself, as well as all their hydrogenated derivatives, are commonly found. Piperine (21) from various pepper species is included. Although it is not an alkaloid, it is the earliest and best known of the pungent acid amides. Ricinine (22) from the seeds of the castor plant is also cited because it was for a long time the only naturally occurring nitrile. Trigonelline (23) is another betaine of wide distribution. Its reduction product, arecoline (24), is the most important constituent of the areca (Betel) nut which is widely employed as a masticatory in the far eastern tropical countries. See Table 2 for structures.

The study of the toxic alkaloids of *Conium maculatum* (the notorious hemlock) played a useful part in the development of heterocyclic chemistry. The principal base, coniine (2-*n*-propylpiperidine) was the first of all the alkaloids to be synthesized. Also found were *N*-methylconiine, conhydrine (2-(1-hydroxy-*n*-propyl)piperidine), pseudoconhydrine (2-*n*-propyl-5-hydroxypiperidine), and γ -coniceine (3,4,5,6-tetrahydro-2-*n*-propylpyridine).

From *Lobelia inflata*, 2,6-disubstituted piperidines, some fourteen in all, have been described. All are derived from lobelanine (25) which is synthesized (90% yield) by a route of possible biosynthetic significance.



In addition to simple bases there are more complex alkaloids in tobacco. Many of these alkaloids are derivatives of 2- β -pyridylpyridine. Their isolation is facilitated by their steam volatility in basic media. The most important alkaloid in tobacco is nicotine ($\text{C}_{10}\text{H}_{14}\text{N}_2$) (26), optically inactive. An isomeric alkaloid anabasine (27) is a higher homolog than nicotine. The structure of anabasine was easily proved by hydrogenation to isonicotine ($\text{C}_{10}\text{H}_{12}\text{N}_2$), also a natural product. Nicotine and tobacco are no longer of direct therapeutic interest, although both are employed as veterinary anthelmintics and the former is still used as an insecticide. Nicotine, like several other alkaloids of widely divergent structure, gelsemine (101) and sparteine (42), has the ability to induce a transient stimulation, followed by depression, and finally paralysis of the autonomic ganglia.

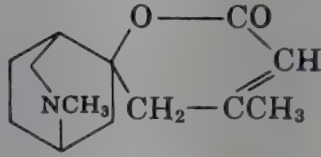
The once reputed heart poison, carpaine (28), from the leaves of *Carica papaya* (pawpaw) is an example of a large-membered ring ester. Gentianine (29), another pyridine alkaloid, is discussed on page 772.



Tropane Alkaloids. The tropane alkaloids can be regarded in many respects as esters of bicyclic derivatives of conhydrine. They are found principally in solanaceous and coca plants as well as in the *Convolvulaceae* and *Dioscoraceae* families. They are esters of an organic acid (atropic, benzoic, cinnamic, isovaleric, α -methylbutyric,

tiglic, tropic, truxillic, and veratric acids) and one of several amino alcohols. The latter are hydroxy derivatives of tropane (30) or its nor compound. Important members are *l*-hyoscyamine (31), atropine (optically inactive) (31), meteloidine (32), scopolamine (33), and cocaine (34). The first two compounds are valued for their mydriatic properties, the last is mainly used as a local anesthetic. Scopolamine is useful as a sedative and for the treatment of sleeping sickness. Dioscorine (35) and pseudopelletierine (36), a pomegranate root bark alkaloid, are, respectively, a variant (18) and a homolog of the tropane heterocycle:

Table 3. Tropane Alkaloids

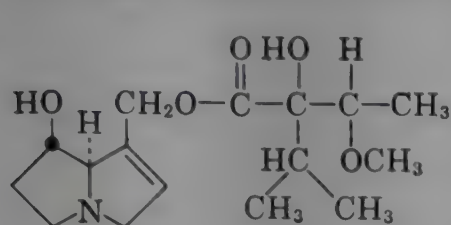
$ \begin{array}{ccccc} \text{H}_2\text{C} & \text{---} & \text{CH} & \text{---} & \text{CH}_2 \\ & & & & \\ & & \text{NCH}_3 & & \text{CH}_2 \\ & & & & \\ \text{H}_2\text{C} & \text{---} & \text{CH} & \text{---} & \text{CH}_2 \end{array} $ <p style="text-align: center;">tropane (30)</p>	$ \begin{array}{ccccccc} \text{H}_2\text{C} & \text{---} & \text{CH} & \text{---} & \text{CH}_2 & & \text{CH}_2\text{OH} \\ & & & & & & \\ & & \text{NCH}_3 & & \text{CH} & \text{---} \text{OCO} & \text{---} \text{CH} \\ & & & & & & \\ \text{H}_2\text{C} & \text{---} & \text{CH} & \text{---} & \text{CH}_2 & & \text{C}_6\text{H}_5 \end{array} $ <p style="text-align: center;"><i>l</i>-hyoscyamine and atropine (31)</p>	
$ \begin{array}{ccccccc} \text{HOCH} & \text{---} & \text{CH} & \text{---} & \text{CH}_2 & & \\ & & & & & & \\ & & \text{NCH}_3 & & \text{CH} & \text{---} \text{OCOC} & \text{---} \text{CH} & \text{CH}_3 \\ & & & & & & \\ \text{HOCH} & \text{---} & \text{CH} & \text{---} & \text{CH}_2 & & \text{CH}_3 \end{array} $ <p style="text-align: center;">meteloidine (32)</p>	$ \begin{array}{ccccccc} \text{HC} & \text{---} & \text{CH} & \text{---} & \text{CH}_2 & & \text{CH}_2\text{OH} \\ & & & & & & \\ \text{O} & \diagup & & \diagdown & & \text{NCH}_3 & & \text{CH} & \text{---} \text{OCO} & \text{---} \text{CH} \\ & & & & & & \\ \text{HC} & \text{---} & \text{CH} & \text{---} & \text{CH}_2 & & \text{C}_6\text{H}_5 \end{array} $ <p style="text-align: center;">scopolamine (33)</p>	
$ \begin{array}{ccccccc} \text{H}_2\text{C} & \text{---} & \text{CH} & \text{---} & \text{CHCOOCH}_3 \\ & & & & \\ & & \text{NCH}_3 & & \text{CHOCOC}_6\text{H}_5 \\ & & & & \\ \text{H}_2\text{C} & \text{---} & \text{CH} & \text{---} & \text{CH}_2 \end{array} $ <p style="text-align: center;">cocaine (34)</p>	 <p style="text-align: center;">dioscorine (35)</p>	$ \begin{array}{ccccccc} \text{H}_2\text{C} & \text{---} & \text{CH} & \text{---} & \text{CH}_2 \\ & & & & \\ & & \text{NCH}_3 & & \text{C=O} \\ & & & & \\ \text{H}_2\text{C} & \text{---} & \text{CH} & \text{---} & \text{CH}_2 \end{array} $ <p style="text-align: center;">pseudopelletierine (36)</p>

Senecio Alkaloids. Since the genus senecio still provides the greatest number of species containing alkaloids with a hydroxylated pyrrolizidine moiety, the term "senecio alkaloids" is generally used to describe this class. Pyrrolizidine alkaloids have been isolated from many different genera of the families *Compositae*, *Leguminosae*, and *Boraginaceae*. One feature of interest relating to the pyrrolizidine alkaloids is the wide occurrence of *N*-oxides. Apart from the *N*-oxide possibility, the bases fall into three main categories, monoesters (37) of the necine (alkanolamine portion) with a monocarboxylic necic acid, diesters (38) of the necine with two different monocarboxylic necic acids, and cyclic esters (39) of the necine with a dicarboxylic necic acid. The last group represents compounds containing rings of eleven to twelve members. The acids range in size from C₅ (angelic acid) to C₁₀ (senecic acid). These alkaloids are no longer used in modern medicine. Practical interest in them arises from the fact that they cause disease in farm animals kept in pastures infested with senecio species. The bases vary in degree of toxicity but a characteristic feature of the group is the production of liver necrosis.

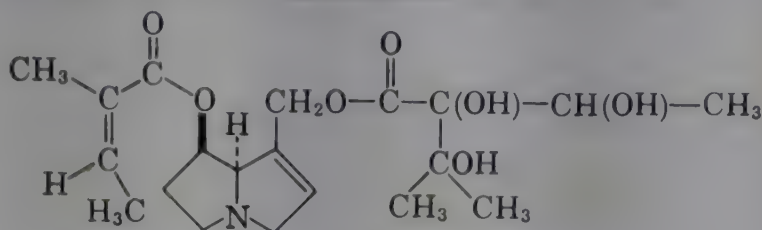
Lupin Alkaloids. The lupin alkaloids may also be referred to as the quinolizidine alkaloids, indicating the chemical denominator common to most of them. They are isolated principally from plants of the family *Papilionaceae*. As in the case of the

senecio alkaloids, *N*-oxides are also found here. The alkaloid content of various genera and species within the *Papilionaceae* continues to be of interest because of the fine balance between consumption as fodder and danger as a poison. Several plants, notably laburnum (*Cytisus laburnum*), have been the cause of fatal poisoning probably due to their cytisine (40) content. Other representatives of this large group are lupanine (41), sparteine (42), lupinine (43), and matrine (44).

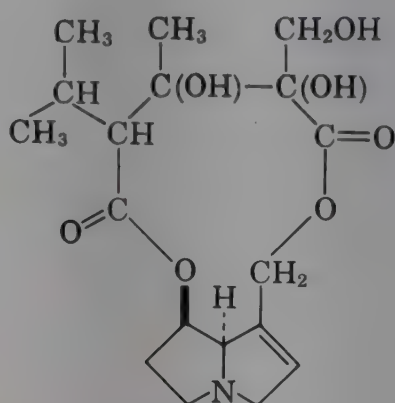
Table 4. Senecio and Lupin Alkaloids



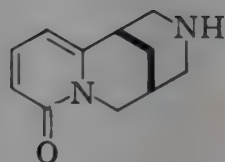
heliotrine (37)



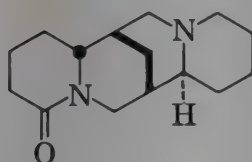
echimidine (38)



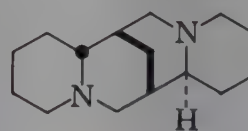
junceine (39)



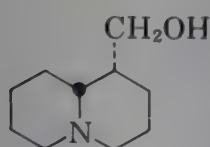
cytisine (40)



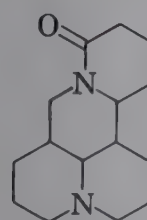
lupanine (41)



sparteine (42)



lupinine (43)



matrine (44)

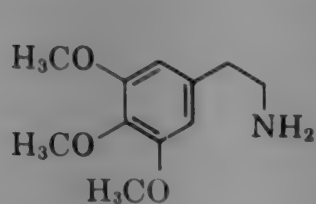
Isoquinoline and Related Alkaloids. By far the largest number of known alkaloids are derived from hydroxylated phenylalanines and their corresponding β -phenylacetaldehydes, and occur especially in the *Fumariaceae*, *Papaveraceae*, *Ranunculaceae*, *Rutaceae*, and *Berberidaceae* families. The wide range of structures which result are conveniently subdivided as follows: β -phenylethylamine, simple isoquinoline, benzylisoquinoline, phthalide-isoquinoline, cularine, aporphine, alkaloids related to berberine, α -naphthaphenanthridine, amaryllidaceae and erythrina alkaloids, and cryptopleurine.

Table 5. Isoquinoline and Related Alkaloids

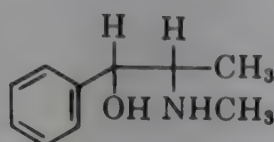
papaverine (48)	laudanosine (49)	cularine (50)
bulbocapnine (51)	morphine (52) (R = H) codeine (R = CH ₃)	hydrastine (53)
canadine (54)	berberine (55)	cryptopine (56)
chelidonine (57)	chelerythrine (58)	
pilocereine (59)		

Among simple amines, β -phenylethylamine itself is found in many species of acacia and in mistletoe. Hydroxylated derivatives are common and mescaline (45) from anhalonium species of cacti is known for its central nervous system effects, especially the production of color vision in susceptible persons. The Chinese drug "Ma-Huang" (*Ephedra sinica*) is the source of valuable sympathomimetic drugs, the most important of which is ephedrine (46), now made synthetically.

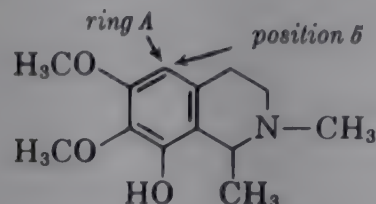
The isoquinoline alkaloids (see Table 5) without exception contain at least two oxygen atoms at positions 6 and 7 in ring A (see 47). The appearance of a third oxygen in the same ring is frequent but never at the 5 position. One of the simplest of these alkaloids is pellotine (47) which co-occurs with the β -phenylethylamines in cacti.



mescaline (45)

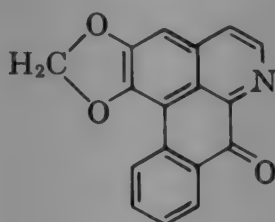


ephedrine (46)

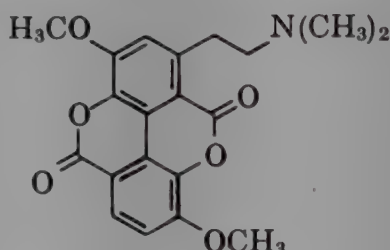


pellotine (47)

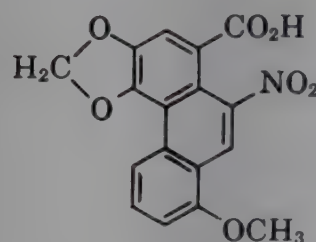
Historically, the opium alkaloid papaverine (48) was the first benzyloisoquinoline to be recognized in nature and the first of these to be synthesized, but it is not truly representative of the group which includes 1,2,3,4-tetrahydroisoquinolines, eg, co-occurring, laudanosine (49). A further cyclization of benzyloisoquinoline can give rise to either the seven-membered ring derivative, cularine (50), or to the aporphines. The most important member of this class is bulbocapnine (51) which can induce a state of catalepsy. Bulbocapnine has been used in treatment of diseases in which involuntary movement is a symptom, such as paralysis agitans and St. Vitus dance. Some other alkaloids and natural products are considered to be products of further oxidation of the aporphine system. They are liriodenine (60) from the yellow poplar (*Liriodendron tulipifera*) (19), taspine (61) from *Leontice eversmanni*, and aristolochic acid (62) from *Aristolochia siphon* (20).



liriodenine (60)



taspine (61)



aristolochic acid (62)

Cyclization of the benzyloisoquinoline system can occur in another very important way which leads to morphine (52) and codeine (52). These alkaloids, because of their analgesic and euphoric properties, have widespread medicinal and illicit uses. Morphine is by far the most important of the forty-odd alkaloids obtained from the opium poppy (*Papaver somniferum*). Because of the addicting properties, an immense amount of work has been directed towards the isolation or synthesis of a nonaddicting analgesic, but so far this has been without success.

Addition of one carbon to the benzyloisoquinoline moiety yields lactones, such as hydrastine (53), and the tetracyclic heterocycle dibenzo(a,g)quinolizidine (protoberberine) skeleton. Representative examples are canadine (54) which is found, along with hydrastine, in *Hydrastis canadensis*; the quaternary, berberine (55), from barberry (*Berberis vulgaris*); and cryptopine (56), from opium; as well as corydalis and dicentra species. Berberine is bitter but not too toxic and is often used in the preparation of bitter tonics.

If the B ring in the protoberberine skeleton (54) is opened at the dotted line and reclosed on carbon 13, 1,2-benzophenanthridine (α -naphthaphenanthridine) heterocycle is generated. Two alkaloids characteristic of this small group are chelidonine

(57) from *Chelidonium majus* and chelerythrine (58) from blood root (*Sanguinaria canadensis*) and other papaveraceous plants. These alkaloids are not known to have any marked physiological activity but if the report that sanguinarine is the causal agent of glaucoma among peasants in India is true, this estimate would have to be revised (21).

Dimeric and trimeric isoquinoline alkaloids are known in large number and are formed by oxidative coupling of phenolic monomers. A simple example is pilocereine (59) from the giant cacti, *Lophocereus schottii* and *Pachycereus marginatus*. A more complicated type is illustrated by isotrilobine (63) from cocculus species. The quaternary alkaloid tubocurarine chloride (64) represents another mode of coupling. It is the usefully active agent of tube curare whose source is now known to be various chondrodendron species (especially *Chondrodendron tomentosum*). The drug is used as an adjunct in surgical anesthesia.

Several groups of alkaloids are derived via oxidative cyclization of derivatives of hydroxylated β -phenylethylamines or equivalent systems. Thus are generated the erythrina alkaloids (65,66) and the amaryllidaceae alkaloids (67-71), in which these

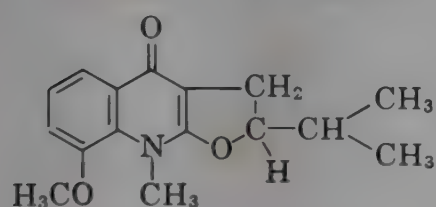
Table 6. Bisbenzylisoquinoline, Erythrina, and Amaryllidaceae Alkaloids

isotrilobine (63)	tubocurarine chloride (64)	erythraline (65)
α -erythroidine (66)	lycorine (67)	tazettine (68)
galanthamine (69)	crinine (70)	belladine (71)

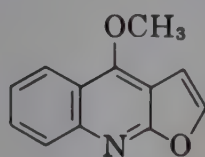
residues are easily seen, as well as cryptopleurine (118) whose genesis is not quite so obvious. The latter alkaloid has powerful vesicant properties. The erythrina bases are curarizing agents of high potency which, unlike the curare alkaloids, are tertiary and orally effective. The amaryllidaceae alkaloids are of interest not only because of the new heterocyclic systems which were discovered but also because most of these plants are grown for their beauty. Lycorine (67) and tazettine (68) are the major alkaloids of the daffodil and snow drop, respectively. Galanthamine (69) has useful anticholinesterase activity. As expected from its resemblance to morphine, crinine (70) has good analgesic properties but is too toxic for use. The simplest alkaloid of this class is belladine (71) whose nor compound has been shown to be a true precursor of galanthamine (22). Table 6 shows the structures of these alkaloids.

Quinoline Alkaloids. In the same way that a wide variety of alkaloids are derived from hydroxylated phenylalanines, a large number of different compounds arise from tryptophan and its precursors, indole and anthranilic acid. Some of the "alkaloids" produced from anthranilic acid are vinylogous amides, such as echinopsine (*N*-methyl-4-quinolone) from *Echinops vitro*, 2,3,4-trimethoxy-10-methylacridone from *Evodia alata*, and lunacrine (72) found in lunaria species. Compounds similar to the latter, the simplest being dictamine (73), are found in the genera *fagara skimmia*, *orixa*, *chloroxylon*, and *balfourodendron*. The bitter taste of *Angostura* (*Galipea officinalis*) is due to its alkaloid content; the principal base is cusparine (74). Anthranilic acid, or more probably the aldehyde, is involved in the formation of vasicine (75) from *Peganum harmala* as well as the more complicated quinazoline, febrifugine (76), the antimalarial alkaloid of the horticultural hydrangea (*Dichroa febrifuga*). Finally, the alkaloids cryptopleine (77) from cryptolepis species and rutaecarpine (78) from

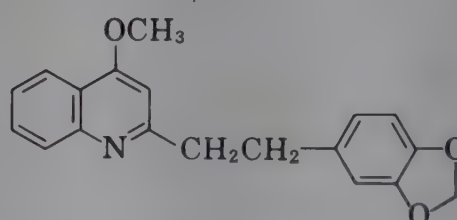
Table 7. Alkaloids Derived from Anthranilic Acid



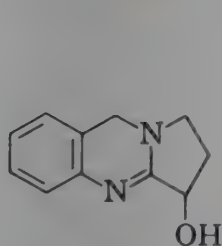
lunacrine (72)



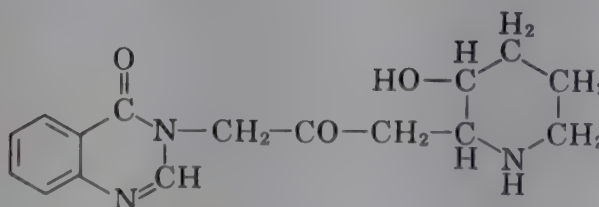
dictamine (73)



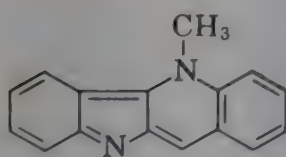
cusparine (74)



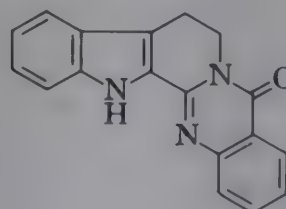
vasicine (75)



febrifugine (76)



cryptopleine (77)



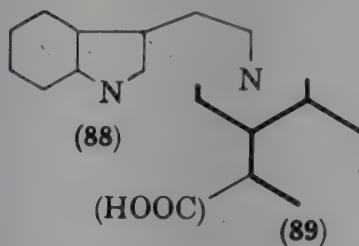
rutaecarpine (78)

Evodia rutaecarpa are cases in which an anthranilic acid equivalent has condensed with an appropriate indole. Table 7 gives the structures of the alkaloids derived from anthranilic acid.

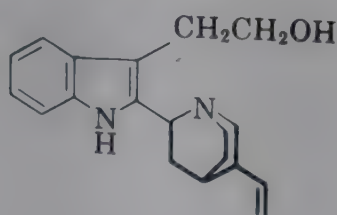
Indole Alkaloids. Indole alkaloids range in complexity from simple derivatives, gramine (79) from barley mutants and *Arundo donax* (Asiatic reed), and hypaphorine (80) from erythrina species, to the complexity of the "dimeric" alkaloids such as toxiferine (94). Co-occurring with vasicine (75) in *Peganum harmala* are harmaline (81) and harmine (82). The latter is the active principle of the South American narcotic drug, yage, also called caapi, or ayahusca (*Banisteria caapi*).

The Calabar bean (*Physostigma venenosum*), long used in West Africa as an ordeal poison, contains as the active agent the useful anticholinesterase inhibitor, physostigmine (83) or eserine. See Table 8 for the structures of the indole alkaloids.

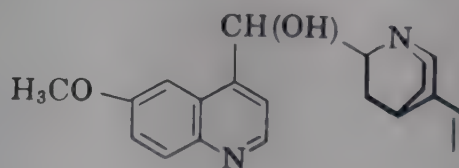
By far the greatest number of indole alkaloids, especially plants of the *Apocynaceae*, *Rubiaceae*, and *Loganiaceae* families are derived from a tryptamine residue (88) and a ten-carbon unit (89) (dark type in Tables 8 and 9), which seem to be able to combine in a wide variety of ways. This C₁₀ fragment, which is responsible for all the carbons of gentianine (29) from the gentian family as well as the core of the amoebicidal



alkaloid emetine (92) from the Brazilian *Cephaelis ipecacuanha*, is shown in heavy type. The two major routes of condensation are the α -type, for example, yohimbine (84), and the β -type, illustrated by the Wieland-Gumlich aldehyde (85) and the poison, strychnine (86), from *Strychnos nux vomica*. There are many isomers of yohimbine, a supposed aphrodisiac, all of which have one feature in common, namely the same absolute stereochemistry at the starred carbon in 84. This appears to be a common stereochemical denominator for all complex indole alkaloids. Cinchonamine (90) from many cinchona plants provides the clue which suggests that alkaloids, such as the co-occurring cinchona base, quinine (91), are actually derived by rearrangement of indoles, such as 90. Quinine, long used for the treatment of malaria, was displaced

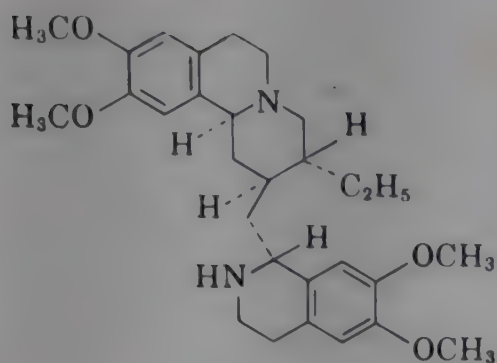


cinchonamine (90)

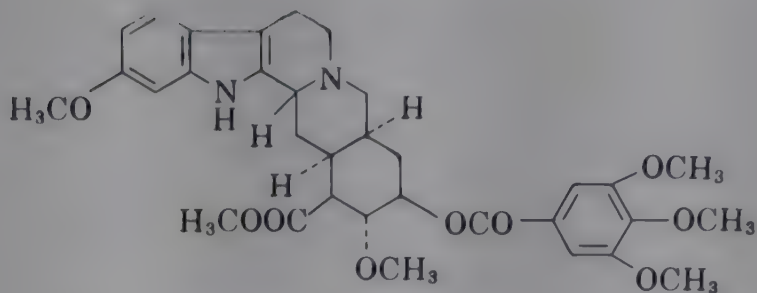


quinine (91)

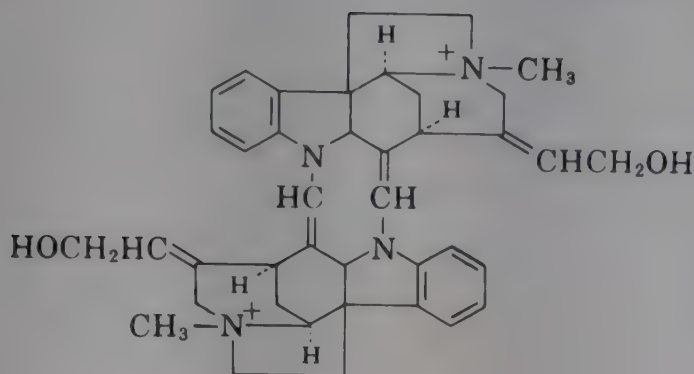
during World War II when true prophylactics became synthetically available. Today it is often used when a bitter taste is desired. A diastereoisomer of quinine, quinidine, is used to control auricular fibrillation. *Rauwolfia serpentina* provides by far the most important indole alkaloid, reserpine (93). The clinical use of reserpine has revolutionized the control of hypertension, and up to the present time it is the most valuable natural drug to have been discovered. For this reason so much effort has been put into the study of plant extracts, especially indole alkaloids, in present years. The



emetine (92)



reserpine (93)



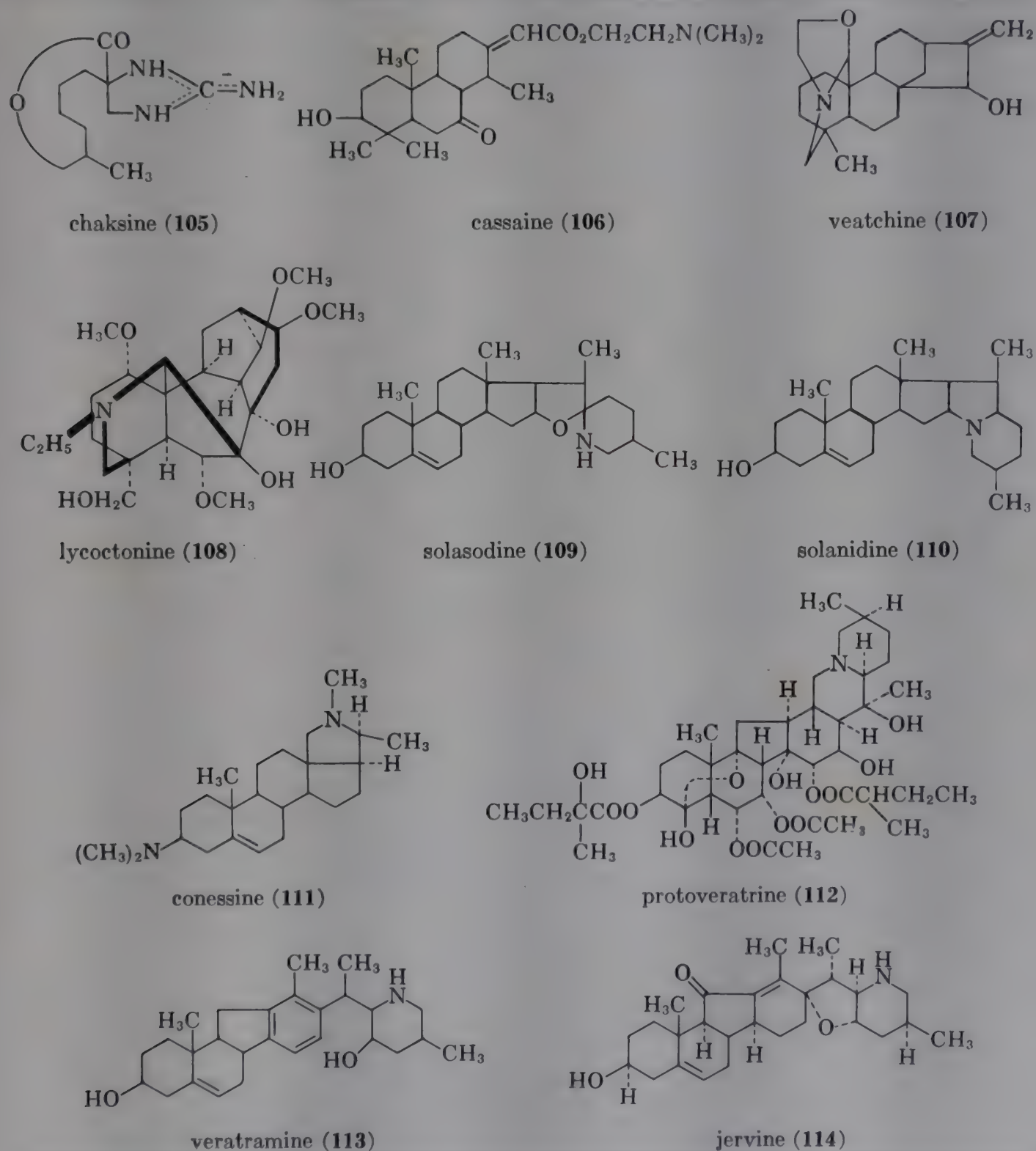
toxiferine (94)

major alkaloid of many rauwolfia plants is ajmaline (87) which finds some use, like quinidine, in the treatment of auricular fibrillation. Further variations in structure of α -type indoles are ajmalicine (95) and the oxindole, rhyncophylline (96). Then there are the more highly aromatized bases from the alstonia species, alstoniline (97) and alstonidine (98). Many indole alkaloids have proved difficult to degrade by normal methods. These include ibogaine (5) from *Tabernanthe iboga*, the source of the central nervous system stimulant of the Congo natives; aspidospermine (99) from *Aspidosperma quebracho* bark; eburnamonine (100) from *Hunteria eburnea*; and gelsemine (101) from the Carolina jasmine, *Gelsemium sempervirens*. A further variation is possible if the C_{10} residue (89) plus ammonia condenses with indole itself to give rise to the aspidosperma bases, uleine (102) and olivacine (103). By far the most complex bases are the dimeric alkaloids, many of unknown structure; the most thoroughly investigated ones are among sixty-odd alkaloids isolated from calabash curare, the principal plant source being *Strychnos toxifera*. This group of dimeric compounds is quaternary and can be considered to arise by a doubling of the Wieland-Gumlich aldehyde (85) metho salt. They are curarizing agents; the safest one for human use is toxiferine (94), which is now synthesized on a commercial basis. The dimeric alkaloid, vincaleucoblastine (104), from *Vinca rosea* (periwinkle) has tumor-inhibiting properties.

Terpenoid and Steroidal Alkaloids. The final major class of alkaloids to be considered are those which are generated by the involvement of nitrogen in the biosynthesis of the terpenoids and steroids. Thus, chaksine (105) from *Cassia absus* (*Leguminosae*) can be thought of as a monoterpenoid alkaloid whereas telepogine (4) and cassaine (106) are examples of diterpenoid alkaloids. The latter alkaloid (23) is a constituent of sassay bark (*Erythrophloeum guineense*), formerly used as an ordeal poison in West Africa. A different diterpenoid type is shown by veatchine (107) from *Garrya veatchii*. It is the simplest of all the aconite and delphinium alkaloids; the most complicated of these resembles lycotone (108). Steroidal alkaloids occur

widely in the genera *solanum*, *veratrum*, and *holarrhena*. The former are normally isolated as glycosides; the most well-known examples are solmargine (solasodine (109) plus trisaccharide of two D-glucose residues and L-rhamnose) from *Solanum marginatum* and α -solanine (solanidine (110) plus trisaccharide of L-rhamnose, D-glucose, and D-galactose) from *Solanum sodomium* (Dead Sea apple). In the *holarrhena* alkaloids the heterocyclic portion is different; conessine (111) with two nitrogens is typical of this group. In the *veratrum* (sabadilla) group, the steroidal skeleton has undergone some rearrangement. The crude alkaloids from *Veratrum viride* show good intravenous hypotensive properties. The best of the pure compounds is protoveratrine A (112) but the therapeutic dose is very close to the emetic dose. A great deal of partial synthetic

Table 9. Terpenoid and Steroidal Alkaloids

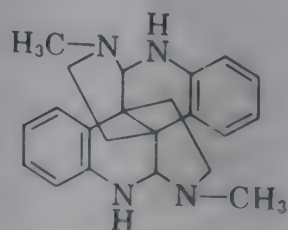


work to prepare derivatives with more desirable properties has not been successful (24). The remaining structural variations are illustrated by veratramine (113) and jervine (114). Table 9 shows the structures of the terpenoid and steroidal alkaloids.

Table 10. Alphabetical List of Alkaloids and Structure Numbers

ajmalicine (95)	cryptopine (56)	isotrilobine (63)	quinine (91)
ajmaline (87)	cryptopleurine (118)	jervine (114)	reserpine (93)
akuammicine (7)	cularine (50)	junceine (39)	rhyncophylline (96)
alstonidine (98)	cuskohygrine (20)	laudanosiene (49)	ricinine (22)
alstoniline (97)	cusparine (74)	liriodenine (60)	rutaecarpine (78)
anabasine (27)	cytisine (40)	lobelanine (25)	samandarine (2)
annofoline (12)	dehydrobufotenine (1)	lunacrine (72)	scopolamine (33)
annotinine (14)	dictamine (73)	lupanine (41)	solanidine (110)
arecoline (24)	dioscorine (35)	lupinine (43)	solasodine (109)
aristolochic acid (62)	eburnamonine (100)	lycoctonine (108)	sparteine (42)
aspidospermine (99)	echimidine (38)	lycodine (13)	stachydrine (18)
atropine (31)	emetine (92)	lycorine (67)	strychnine (86)
belladine (71)	ephedrine (46)	lysergic acid amide (9)	taspine (61)
berberine (55)	ergotamine (8)	matrine (44)	tazettine (68)
bulbocapnine (51)	erythraline (65)	mescaline (45)	telepogine (4)
caffeine (16)	α -erythroidine (66)	meteloidine (32)	toxiferine (94)
calycanthine (115)	febrifugine (76)	morphine (52)	triacanthine (17)
canadine (54)	galanthamine (69)	muscarine (11)	trigonelline (23)
carpaine (28)	gelsemine (101)	nicotine (26)	tropane (30)
cassaine (106)	gentianine (29)	olivacine (103)	tropinone (7a)
chaksine (105)	gramine (79)	palustrine (15)	tubocurarine
chelerythrine (18)	harmaline (81)	papaverine (48)	chloride (64)
chelidonine (57)	harmine (82)	pellotine (47)	uleine (102)
cinchonamine (90)	heliotrine (37)	physostigmine (83)	vasicine (75)
cocaine (34)	himgravine (117)	pilocarpine (116)	veatchine (107)
codeine (52)	hydrastine (53)	pilocereine (59)	veratramine (113)
colchicine (3)	hygrine (19)	piperine (21)	vincaleucoblastine (104)
conessine (111)	hyoscyamine (31)	protoveratrine (112)	Wieland-Gumlich
crinine (70)	hypaphorine (80)	pseudopelletierine (36)	aldehyde (85)
cryptolepine (77)	ibogaine (5)	psilocybine (10)	yohimbine (84)

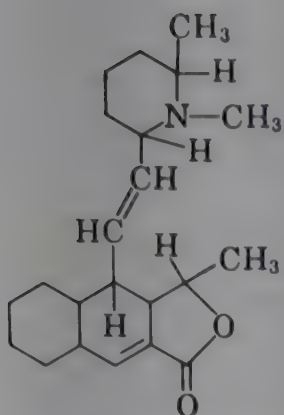
Miscellaneous. Among miscellaneous alkaloids not dealt with under any of the above classifications are calycanthine (115), from *Calycanthus floridus* (Carolina allspice), which is thought to arise by dimerization and rearrangement of *N*-methyl-tryptamine; cryptopleurine (118); glyoxaline bases, such as pilocarpine (116); and the very peculiar compounds represented by himgravine (117) from *Himatandra baccata* (25). Pilocarpine from various pilocarpus species (jaborandi) is used as a miotic in the treatment of glaucoma.



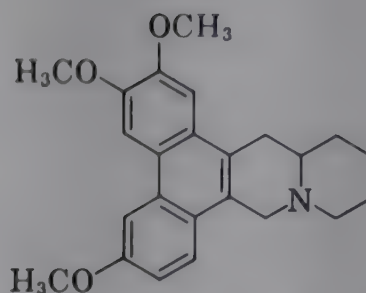
calycanthine (115)



pilocarpine (116)



himgravine (117)



cryptopleurine (118)

As the pace of modern chemical research has increased, the rate of discovery of new types of alkaloid structures has also increased. It is for this reason that greater stress has been placed in the above discussion on the origin of the different heterocyclic systems so that the relationship between established facts and findings yet to be made will be more readily apparent.

Table 10 gives a complete listing of the alkaloids discussed in this article.

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HISTORY, PREPARATION, AND USE

The alkaloids—withstanding the advent of antibiotics and of many new and valuable synthetic drugs—still constitute an indispensable part of our medicinal arsenal. Their manufacture, consequently, comprises an important segment of the fine chemicals industry. The production of alkaloids is steeped in tradition, because processes are so highly specialized that it frequently takes years for them to become established on an economical basis.

For a pertinent discussion of sources of botanical drugs and the influence of current events on them the reader is referred to a recent paper by Woodward (1).

The following list is designed to indicate the degree of use of various alkaloids by U.S. physicians:

Major. Rauwolfia (reserpine, etc), codeine, atropine, ergonovine, morphine, quinidine, methylergonovine, pilocarpine, ephedrine.

Medium. Scopolamine, papaverine, colchicine, quinine, lobeline, hyoscyamine, ergotamine, cocaine.

Minor. Strychnine, protoveratrine, physostigmine, dihydroergotoxine, emetine, tubocurarine, vincalcalcin.

Total alcoholic extracts are recognized in the pharmacopeias of many countries and are still widely prescribed in medicine. While it may be believed that they contain all of the activity, either alkaloidal or nonalkaloidal, their use has been decried by pharmacologists. The ultimate goal of the industry is to produce the pure active ingredient void of any toxic or inactive impurities. The following discussion first describes certain processes of general applicability and then gives details of processes for individual alkaloids used in medicine today. The products are presented in the order of their botanical groupings. This account is not to serve as a laboratory manual from which various products can be prepared merely by following printed directions, but rather as a collection of the most promising commercial methods available for the alkaloids discussed. For specific details, reference should be made to the original works cited.

General Procedures

Although the commercial production of any alkaloid is an individual problem, there exist several standard techniques for the preliminary extraction from the drug (the plant material) and for the subsequent separation and purification of the specific alkaloid. Unfortunately, few plants yield single alkaloidal products, so that the main problem involved is separation from usually very complex alkaloidal mixtures. Most approaches fail to take advantage of the relative basicities of the alkaloids during extraction and treat the problem in two steps, isolation and purification. However, these steps are inherently related, and introducing purification methods early in the extraction stages can often be advantageous.

Extraction. *In one general method* for extraction and subsequent purification *water or alcohol is used*, either alone or mixed with dilute acid, usually acetic, hydrochloric, or sulfuric. Aqueous extracts present the disadvantage that their subsequent processing is rather tedious. Such extracts contain both organic and inorganic salts, are usually difficult to filter, foam excessively during concentration, may be subject to fermentation, and almost always lend themselves readily to the formation of difficult emulsions with immiscible organic solvents.

When alcohol is used as the solvent, it is often necessary first to defat the drug with a petroleum solvent. Defatting is especially important with seeds and sometimes with leaves, but is rarely necessary with the bark or roots. Although alkaloids are in general not soluble in the petroleum solvent used for defatting, they sometimes have enhanced solubility in a solution of fat in the solvent. The extract should therefore be checked for the presence of alkaloids with any of the commonly used alkaloidal reagents. This extraction of fat-soluble alkaloids may be desirable, as is the case with lochnericine from *Vinca rosea* Linn. (2). If it is undesirable, it can be prevented by first treating the drug with a strong acid or acid salt to bind the alkaloids in the drug as salts, as has been done in the extraction of ergotamine (3) from ergot. The use of alcohol removes both the alkaloids and their salts, accompanied by a miscellany of pigments, sugars, other organic compounds, and inorganic salts.

In a second general method for extraction *ammonia is used* to alkalinize the drug, thus converting the salts to the free bases. The drug is subsequently extracted with a suitable organic solvent, such as ether, chloroform, or benzene. In many cases the desired alkaloid is heat-labile, and it is essential to select a low-boiling solvent.

Selective Extraction. The procedures described above aim at extracting all of the alkaloids contained in the plant. This usually leads to the production of a very complex mixture and unnecessarily complicates the purification procedures which must follow. The following procedure by Svoboda, designed for both investigational and commercial use, has worked well for a number of plants of the *Apocynaceae* (2,4,5). The process consists essentially of separating the plant alkaloids into those whose tartrates are soluble in organic solvents and those which remain insoluble under the same conditions. Extraction of the weak bases from the crude defatted drug is accomplished with benzene, after the drug has first been pretreated with a solution of 2% tartaric acid. The drug is then made alkaline with ammonia, and the somewhat stronger bases are extracted with benzene. A final extraction of the alkalinized drug with alcohol yields the still stronger bases, such as phenolic and quaternary. (Phenolic bases, containing a hydroxyl function as well as a basic nitrogen, are amphoteric and may therefore act as strong bases, particularly as regards difficulty in extraction.)

Purification of the Extract

Purification of a crude alkaloidal extract can be effected by any of a number of conventional methods, and there is no one procedure to which all alkaloidal mixtures will yield.

Direct Crystallization. This is the simplest procedure, but it seldom succeeds when a crude mixture is involved. It can be very useful, however, when preliminary purification has been effected during extraction of the drug. The extract is evaporated to dryness and the residue is dissolved in a crystallizing solvent, which may be either a single organic solvent, usually methanol or acetone, or a mixture of organic solvents. Solvent combinations most often used are methanol-chloroform, ethanol-chloroform, ethanol-acetone, methanol-ether, methanol-acetone, and methanol-ethyl acetate. On partial evaporation of the solvent, in some cases the pure base may crystallize out.

In other cases advantage can be taken of relative solubilities in different organic solvents, and the pure base may be obtained by the addition of another solvent to the dried extract. The general order of increasing solubilities of most alkaloids is as follows: hexane, benzene, ether, ethyl acetate, methanol, acetone, chloroform, and dioxane.

Steam Distillation. This method can be used only in rare cases. The notable examples of this are coniine, nicotine, and sparteine.

Crystallization of Sparingly Soluble Salts. The choice of acid to be used in salt formation is almost unlimited, but those finding the most widespread use are hydrochloric, hydrobromic, oxalic, picric, perchloric, sulfuric, maleic, tartaric, and ethanesulfonic acid.

The procedure generally followed for the hydrohalides involves dissolving the crude base in methanol or acetone and adding an ethereal solution of the acid. The crude salt generally precipitates in an amorphous form and may be readily crystallized from acetone or acetone-methanol mixtures. Many hydrochlorides are soluble in chloroform to varying degrees, and advantage may be taken of this property to afford a separation. Oxalates, picrates, and perchlorates are usually formed by mixing methanolic solutions of the base and acid. If crystallization does not occur from the reaction mixture, a pasty amorphous mass can be isolated by the addition of ether, and the excess of reagent can be removed by repeated trituration with ether. These salts often crystallize from acetone-water or acetone-ethyl acetate mixtures. Maleates, tartrates, and ethanesulfonates can be prepared in an analogous manner, and can usually be crystallized from either methanol or ethanol. Sulfates or bisulfates are formed with dilute sulfuric acid, and the reaction may be carried out in either aqueous or ethanolic solutions. These salts may be crystallized from water, methanol, or ethanol.

Distribution Between Immiscible Solvents. The alkaloids are taken up in a dilute acid solution. From this, it may be possible to recover the alkaloids simply by the addition of ammonium hydroxide, but it is usually more convenient to extract with a water-immiscible organic solvent. The choice of organic solvent for this method is usually limited to benzene, chloroform, or ether. Upon occasion, it may be found that chloroform produces changes in the alkaloids, and the use of ethylene dichloride is to be preferred.

Gradient pH. This method utilizes the relative basicities of the alkaloids. The pH of an acid solution of the alkaloids is raised by predefined increments, and the

precipitated alkaloids may be isolated by either filtration or extraction with an immiscible solvent. The first fractions will contain the weakly basic alkaloids, the last fractions, the more strongly basic. Solvent extraction is to be preferred to filtration, as the precipitates which form are usually difficult to filter and may well be prone to oxidation when warm moist air is encountered.

The converse of this method can also be employed by successively extracting a benzene, ether, or chloroform extract with small portions of dilute acid, the strongest bases being extracted first. This method is not as flexible as the former, as it is limited in its pH range.

Chromatographic Techniques. Three types of chromatography are usually recognized, viz, adsorption, ion exchange, and partition (see Chromatography).

Although chromatography has been invaluable in the laboratory study of alkaloids, it has not been widely utilized commercially. It has, however, been used for the recovery of hyoscyne, the preparation of the total alkaloids of cinchona, the isolation of morphine and codeine, and the preparation of a number of the oncolytic agents from *Vinca rosea* Linn. In the author's opinion, it is the only technique available for the practical separation of very complex alkaloidal mixtures, and it will find more widespread commercial use as more alkaloids of medicinal value are discovered.

Adsorption Chromatography. A wide choice of adsorbents is available, including alumina, magnesia, silica gel, and carbon. Of these, alumina is finding the widest use. The procedure generally followed involves charging a column of standardized alumina with a benzene solution of the alkaloids to be separated. The column is then developed by successive washing with a series of solvents of increasing eluting power, usually benzene-chloroform mixtures. While advantage may be taken of the ability of some of the colorless alkaloids to fluoresce, any separation based on this will usually be obscured by the presence of colored impurities. Consequently, fractions of appropriate volume are collected, and the presence of the desired alkaloid may be detected by using a suitable color test or by applying any of a number of physicochemical methods. Once detected, the alkaloid may be crystallized directly as the free base or an appropriate salt may be formed.

Ion Exchange Chromatography. The fundamental work on the development of ion exchange resins as a means of separation stemmed from the U.S. atomic energy work. This has been applied to the isolation of scopolamine and quinine by Applezweig (6) and to the morphine alkaloids by Mehlretter and Weakley (7).

Inasmuch as alkaloids possess the property of forming basic cations, they should be capable of being adsorbed from dilute aqueous solution on a cationic exchanger. Any number of such synthetic resins are commercially available. The elution of the ions adsorbed by the resin may be accomplished by displacement with a more strongly adsorbed ion or with highly concentrated solutions of other ions. Ammoniacal alcohol is usually used to recover the free base from the column. The resin can usually be regenerated by washing with an aqueous solution of a dilute mineral acid.

Partition Chromatography. This process involves fractional solvent-solvent extraction on a column packed with hydrated silica precipitates holding approximately 50% water, and developing with water-immiscible solvents. Water or hydroxylated polar solvents are generally used as the stationary solvents while relatively nonpolar solvents act as the mobile phase. This method has found some use in laboratory investigations, but it remains to be developed for commercial application for alkaloidal separations.

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Calabar Bean Alkaloids

The seeds of the vine *Physostigma venenosum* Balf. (*Leguminosae*) have long been used by the natives of West Africa as an ordeal poison (1). The main and most important alkaloid present in the seed, or calabar bean, is called physostigmine. It was first isolated as the amorphous base in 1864 by Jobst and Hesse (2,3); Vee first obtained it in crystalline form and called it eserine (4). Both names are still used to designate the base.

Physostigmine is a parasympathomimetic agent and finds its chief use topically as a miotic in glaucoma. It is usually supplied as the salicylate.

Physostigmine. The preparation of this alkaloid by the usual techniques presents no unusual difficulties. Care should be exercised to avoid heating concentrated solutions of either the base or its salts to prevent the formation of colored decomposition products. The powdered drug is extracted with either warm methanol or warm denatured ethanol. The residue from this extract is dissolved in either ether or ethylene dichloride and the alkaloid is extracted therefrom with 1% sulfuric acid. Coloring matter and other impurities can be removed by extraction of the aqueous acid phase with petroleum ether followed by isopropyl ether. The aqueous phase is made alkaline with sodium carbonate and is then extracted with ether.

The salicylate is prepared by adding an excess of an ether solution of salicylic acid to an ether solution of the base.

The complete synthesis of physostigmine has been accomplished by Julian and Piki (5).

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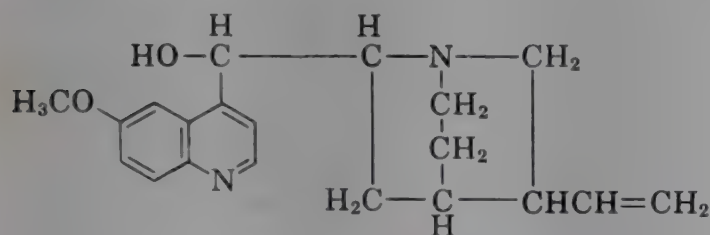
Cinchona Alkaloids

The use of the bark of a certain indigenous tree in Peru by the native medicine men to treat malarial fever was recorded by the Jesuits in 1633. It was supposedly effective in treating the Countess of Chinchon, wife of the Spanish Viceroy to Peru, who was responsible for introducing it into Spain in 1639 for the treatment of ague. By 1640 the drug was used in Europe to treat fevers. It has been referred to as Peruvian, Jesuit's, and Cardinal's bark and was used for almost two centuries as the powdered drug, extract, and infusion (1).

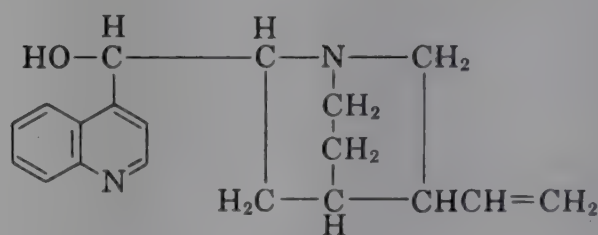
More than thirty alkaloids have been isolated from various species of cinchona and remijia (*Rubiaceae*). Cinchona is the dried stem or root bark of various cinchona species, mainly *C. officinalis* L. (*C. ledgeriana* Moens) cultivated mostly in Java, *C. officinalis* L. (*C. calisaya* Wedd.) from Bolivia, *C. micrantha* R. & P. from Peru, *C. pubescens* Vahl. (*C. succirubra* Pav.) from Ecuador, and *C. pitayensis* Wedd. from Colombia.

The typical actions of cinchona are largely attributable to its quinine content. Cinchona and its galenical preparations are rarely used in therapeutics in the U.S. They are, however, employed in the tropics where malaria is endemic as cheap substitutes for quinine. Elixirs of iron, quinine, and strychnine, and iron, quinine, and strychnine phosphates are widely used, but represent irrational therapeutic survivals. Totaquine is a mixture containing no less than 7% and no more than 12% of anhydrous quinine, and no less than 70% and no more than 80% of total anhydrous crystallizable cinchona alkaloids, the remainder consisting chiefly of diluents. It is cheaper than quinine and is readily available in parts of the world where quinine is expensive or limited in supply.

The most important alkaloids of cinchona are two pairs of stereoisomers, the one being quinine and quinidine and the other, cinchonine and cinchonidine. Neither of the latter pair is employed extensively in modern therapeutics in the U.S.A. Cinchonine shares the same type of therapeutic actions as quinine, but it possesses much weaker antimalarial activity. It is used as a cheap substitute for quinine. Cinchonidine shares the antipyretic and analgesic effects of quinine and approaches its antimalarial potency.



quinine, quinidine



cinchonine, cinchonidine

Quinine. Quinine was first prepared in pure form by Pelletier and Caventou (2), by resolving the crystalline mixture "Cinchonino" of the Spanish physician Gomez into quinine and cinchonine. One widely used method for extracting the bark involves intimate mixing with freshly slaked lime, followed by moistening with a dilute aqueous solution of either sodium hydroxide or carbonate. Extraction is then effected with hot mineral oil. The alkaloids are extracted from the oil with dilute sulfuric acid, and crude quinine sulfate is obtained by neutralizing the acid solution with dilute sodium hydroxide. Purification can be achieved by recrystallizations from hot water slightly acidified with sulfuric acid.

Detailed procedures involving the use of a calcium hydroxide solution and extraction with benzene are given by Schwyzer (3).

An unusual and promising approach is the use of an ion exchange process as described by Applezweig and Ronzone (4,5). Extraction is made with 0.1N sulfuric acid, from either dried or fresh bark. The aqueous acid extract is forced upward through Zeo-Karb, a sulfonated coal cation exchanger. When the column is filled to capacity, the exchanger is regenerated with 0.5N sodium hydroxide, followed with water. The water serves to remove a great deal of coloring matter.

After alkali regeneration, the resin is stripped of alkaloids with ethanol. The alkaloid concentrate is dissolved in 1N hydrochloric acid. The pH is adjusted to 6.5 with alkali, and coloring matter and other extraneous material is precipitated and filtered off. Further adjustment of pH, to a point where a heavy white floc precipitates, yields totaquine. This can then be used as a starting source for the desired alkaloids.

The complete laboratory synthesis of quinine was achieved by Woodward and Doering (6). The procedure is too complex and costly to compete with quinine obtained from the natural sources.

Quinine is rarely employed alone as an antimalarial, except in areas of the world where the newer synthetic antimalarials are either too costly or unavailable. During World War II the Allied Armed Forces established the superiority of quinacrine over quinine. A valid antimalarial use of quinine is its combination with a synthetic 8-aminoquinoline derivative for the radical cure of relapsing vivax malaria.

Quinine is still widely used as an analgesic and antipyretic for the relief of headache, neuralgia, etc. In this respect it has the same general usefulness as the salicylates but is somewhat less effective.

Quinine is available as the base and a large number of its salts, viz, bisulfate, dihydrochloride, hydrochloride, phosphate, sulfate, and the relatively tasteless ethyl carbonate and diquinine carbonate. Of the commonly used salts the dihydrochloride and the bisulfate are usually preferred because of their greater solubilities.

Quinidine. This alkaloid was first described by Van Heyningen (7) and was prepared and named by Pasteur in 1853. It is present in cinchona bark to the extent of 0.25–0.30%, especially in *C. pitayensis* and *C. officinalis*, as well as in *Remijia pedunculata*.

It occurs in the quinine sulfate mother liquors and is usually obtained therefrom. It is precipitated with sodium hydroxide solution and is extracted, mixed with cinchonidine, by ether. The cinchonidine is removed as the tartrate, and quinidine hydriodide is precipitated from the mother liquor. It is recovered and recrystallized from ethanol. Quinidine is frequently accompanied by as much as 25–30% of dihydroquinidine. However, the dihydro compound is essentially similar to pure quinidine sulfate in clinical efficacy, duration of action, and toxicity. If required, the dihydro compound can be removed by the mercuric acetate process of Thron and Dirscherl (8).

Quinidine can also be made by the isomerization of quinine (9). This can be accomplished by refluxing under nitrogen with the corresponding sodium alcoholate in absolute 1-butanol, 1-pentanol, 1-hexanol, or 2-heptanol. A quantity of quinidine made in this manner was available during World War II, but it is too expensive to compete with the natural product.

The main use of quinidine is in the prevention or abolition of atrial fibrillation and certain other cardiac arrhythmias. In this respect it is employed much less frequently than digitalis preparations. The preparation most commonly employed is the sulfate, which is administered orally. Occasionally the gluconate is given intramuscularly. When required, the lactate can be used intravenously.

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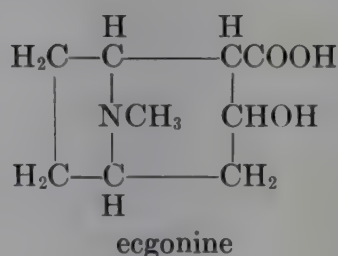
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Coca Alkaloids

Explorers to South America, as early as 1532, found that the natives ascribed a peculiar action to the coca leaf, *Erythroxylon coca* Lam. (*Erythroxylaceae*), namely, that chewing of the leaves increased endurance (1). The principal alkaloid of the various species of erythroxylon is cocaine. Wöhler, who first isolated this alkaloid in 1862 (2), was also the first to observe its peculiar local action.

While cocaine was the first local anesthetic to be discovered, it is now considered too toxic for any anesthetic procedure requiring injection. It is still employed extensively as the hydrochloride in aqueous solutions of 0.1–4% for surface anesthesia in ophthalmology and in solutions of 10–20% for nose and throat work. The base is used in oil solutions and ointments for the same purposes as the salt. Cocaine is a central stimulant but is never employed clinically in this capacity. Addiction and a certain amount of tolerance will result from such use.

Two kinds of coca leaves are available in commerce—Bolivian or Huanuco from *E. coca* Lam. and Peruvian or Truxillo from *E. truxillense* Rusby. Both are cultivated in Java. The South American leaves contain 0.5–1% of total alkaloids, most of which is cocaine. The Javanese drug contains 1.5–2% of total alkaloids, little of which is cocaine; instead, it consists chiefly of ecgonine derivatives, which are subsequently converted to cocaine.



Cocaine is prepared by either the extraction of the South American coca leaves or the conversion of ecgonine obtained by hydrolysis of the total alkaloids of the Javanese leaves, followed by methylation and benzylation by recognized methods (3–7). The ground leaves are alkalinized with an aqueous solution of sodium carbonate and then extracted with a water-immiscible organic solvent, such as benzene. The alkaloids are extracted from the concentrated benzene extract with dilute sulfuric acid. The acid phase is made alkaline and the alkaloids are partitioned into ether. The residue from the ether extract is dissolved in methanol and heated with either sulfuric acid or alcoholic hydrogen chloride. This treatment serves to produce the methyl ester of ecgonine. The reaction mixture is diluted with water and the liberated organic acids are extracted with chloroform. The methyl ecgonine sulfate which can be crystallized from the aqueous phase is benzylation by heating with either benzoyl chloride or benzoic anhydride at 150°C. The cocaine is eventually recrystallized from an acetone–benzene mixture.

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Colchicum Alkaloids

The poisonous nature of the meadow saffron, *Colchicum autumnale* Linn. (*Liliaceae*), is reported to have been known to the physician Dioscorides. The plant is named after the ancient kingdom of Colchis, where it was used in poison potions. It was also referred to as *Hermodactylus* by early writers, and it was recommended for the treatment of gout as early as the sixth and the seventh century (1).

Colchicine is the major alkaloid present in the meadow saffron. It is used extensively as an antiarthritic and in the treatment of acute gout. Its recognized ability to arrest mitosis in the metaphase of plant and animal cells has found important applications in plant genetics for the doubling of chromosomes and in cancer research.

The use of colchicine in treating animals bearing a variety of experimental tumors demonstrates the ability of this drug to modify tumor development, but colchicine generally produces little significant prolongation of survival time. Tumor regression may be noticed only when doses far exceeding those required to arrest mitosis are employed, and these are usually just short of lethal. When regression does occur, it is primarily the result of vascular damage (2).

Colchicine derivatives, viz, desacetylcolchicine, demecolcin, and *N*-desacetylthio-colchicine, exert their greatest effect against myelogenous leukemia. However, they are not considered as reliable as Myleran (3).

Colchicine occurs in all parts of the plant but is usually extracted from either the seeds or the corm. It has been isolated from many colchicum species (4), as well as from a number of other *Liliaceae* (5). The amorphous base was first isolated by Pelletier and Caventou (6), but it was not until some sixty years later that the product was first obtained in crystalline form by Zeisel (7) and Houdès (8). The practical isolation of colchicine is based on the method described by Chemnitius (9). The ground drug is extracted with ethanol. The syrup resulting from concentration of the extract is treated with water, and water-insoluble fats and resins are filtered off. The aqueous phase is then further defatted with petroleum ether. The defatted aqueous solution is then extracted with chloroform, and this extract is concentrated to a gummy residue. Vacuum distillation of either aqueous or ethyl acetate solutions of this residue affords complete removal of the chloroform and yields the crystalline alkaloid. While the ethyl acetate procedure usually results in a lower yield, it is capable of producing a cleaner product.

Colchicine has been synthesized by two groups of independent investigators (10,11) but it is doubtful whether the process developed by either of them will compete with material from the natural source.

Colchicum Glucoside Colchicoside. This glucoside of 3-desmethylcolchicine was first isolated by Bellet (12), and a patent has been issued covering its isolation and

synthesis and the preparation of its acyl derivatives (13). Its reported uses are those of colchicine, but it is less toxic.

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Curare Alkaloids

The word "curare" is believed to have its origin in an attempt by Europeans to approximate phonetically the South American Indian phrase meaning "to kill birds," and it has been used indiscriminately as a generic name for practically all of the South American arrow poisons. Three kinds of curare have been commercially available, each designated by the type of container in which it was packed—tube or bamboo, gourd or calabash, and pot curare. The last is no longer commercially available.

It has been reported (1) that the following *Menispermaceae* from the western Amazonian region are used in preparing the tube or bamboo curare: *Abuta imene* (Mart) Eichl., *A. rufescens* Aubl., *Chondrodendron candicans* (L. C. Rich.) Sandw., *C. iquitum* Diels, *C. limaciifolium* (Diels) Mold., *C. polyanthum* Diels, *C. tomentosum* Ruiz and Pavon, *Telotoxicum minutiflorum* (Diels) Mold., and *T. peruvianum* Mold.

The gourd or calabash curare of the Macusi Indians of British Guiana contains active principles derived from the *Loganiaceae* plant *Strychnos toxifera* Schomb. and this was confirmed by King (2), who isolated from it a quaternary alkaloid indistinguishable from curarine prepared from gourd curare.

The only alkaloid from curare which finds use today is *d*-tubocurarine and it is used as a skeletal muscle relaxant for operative procedures and shock therapy. It is available as the chloride, dimethyl ether chloride, and dimethyl ether iodide. A sterile aqueous solution of curare extract obtained from *C. tomentosum*, biologically standardized to contain 20 units per milliliter, has also been used.

***d*-Tubocurarine Chloride.** Although the free base was isolated earlier in an amorphous form by Boehm (3), this crystalline salt was first prepared by King (4), and several patents covering its preparation have been issued. In one (5), the quaternary base fraction of crude curare of the curine type is obtained by extracting with a dilute aqueous solution of tartaric acid. Inactive contaminants are removed by precipitation with lead subacetate. The filtrate is freed of lead, made alkaline, and

extracted with chloroform to remove the tertiary bases. The picrate is made in the usual manner from the aqueous phase, and this is then converted to the chloride.

Another patent (6) involves adsorption of an aqueous extract of crude curare on activated carbon and elution of the active ingredient with methanol. The picrate is prepared and is passed over an anion-exchange resin impregnated with hydrochloric acid.

O-Dimethyltubocurarine Iodide. This dimethyl ether is easily prepared by dissolving *d*-tubocurarine chloride in methanolic potassium hydroxide and refluxing with an excess of methyl iodide. Clinically, suitable muscle relaxation is obtained with almost no effects on respiration even when excessive amounts are administered.

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Ephedra Alkaloids

The Chinese herb mixture "Ma Huang" has been used empirically by native physicians for more than 5000 years. "Ma Huang," which contains ephedrine, has also been widely used in Russia in the treatment of various disorders.

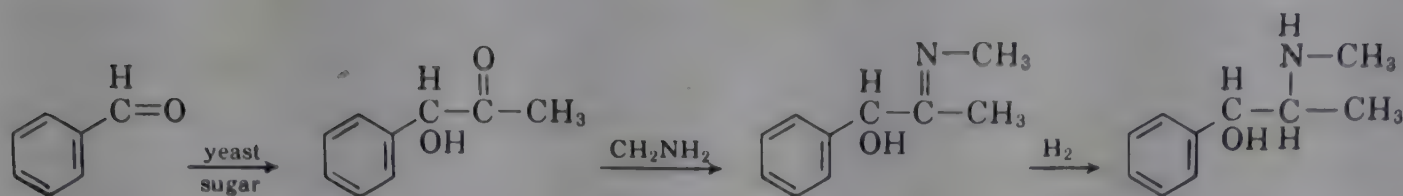
While the mydriatic activity of the alkaloid ephedrine was first demonstrated in 1887 by Miura, the use of ephedrine as a mydriatic enjoyed only a passing vogue. International interest in the drug was stimulated in 1924 by the classical investigations of Chen and Schmidt (1-5), who reported its cardiovascular effects, its similarity to epinephrine, and its absorption from the intestinal tract.

Ephedrine is a sympathomimetic amine used for allergic conditions, CNS (central nervous system) stimulation, and prophylaxis and treatment of hypotension. It is useful as an adjunct to neostigmine in the treatment of myasthenia gravis. Either the sulfate or hydrochloride is used for the systemic effects of the alkaloid. Sterile solutions can be injected subcutaneously, intramuscularly, or intravenously. Topical application to the respiratory or conjunctival mucosa is common. A 0.5-1.0% solution is used as a nasal decongestant; a 4% solution, as a mydriatic. The 1-3% solution of the free base in oil is available for topical use.

***l*-Ephedrine.** The best-known natural source of ephedrine is "Ma Huang." Botanically this herb mixture has been shown to consist of *Ephedra equisetina* Bunge (*Gnetaceae*), *E. sinica* Stapf, and *E. distachya* L. (6,7). Ephedrine was first isolated by Nagai in 1887 (8).

Relatively little ephedrine of commerce is presently obtained by extraction from the plant. Consequently only references to applicable extraction techniques are given (9,10).

A total synthesis and resolution into the optically active bases was first achieved in 1920 by Späth and Göhring (11,12). Many other chemical syntheses have been reported (9), some of which were commercially utilizable.



The most important commercial synthesis of ephedrine is a biosynthetic one in which *l*-ephedrine is produced directly. Neuberg and Hirsch (13) demonstrated that benzaldehyde, when introduced into an actively fermenting sucrose or glucose solution, was reduced by yeast to benzyl alcohol and a phenylpropanolone. Later Hildebrandt and Klavehn (14) showed that the latter compound, *levo*-1-phenyl-2-keto-1-propanol, could be condensed, simultaneously or consecutively, with methylamine and that the condensation product could be reduced to *l*-ephedrine with activated aluminum in moist ether.

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Ergot Alkaloids

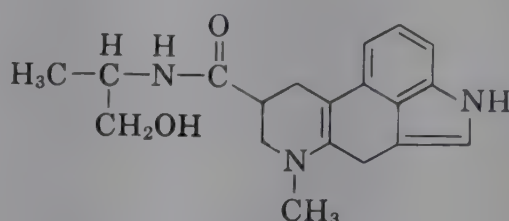
Ergot is the dried sclerotium of *Claviceps purpurea* (Fries) Tulasne (Fam. *Hypocreaceae*) developed on rye plants. It is produced by a fungus growing parasitically on the pistils of many grasses. The commercial ergot of Europe is obtained from rye, while that of the U.S. may be from either rye or wheat. Up until World War II, domestic ergot was merely a curiosity, but because of the shortage of supply and the extreme speculation and contamination to which this commodity was subjected, the domestic source was developed. Attempts to artificially infect rye or wheat have been successful (1), and foreign ergot is now largely obtained from this source.

Ergot is known to contain five physiologically active alkaloids, but only two are used medicinally to any degree, viz, ergotamine and ergonovine. Both have been used as oxytocics to prevent post-partum hemorrhage and to hasten involution of the uterus. Ergotamine is no longer widely used in this respect, its main value now being in the treatment of migraine headache. Ergonovine maleate and the partially synthetic methyl ergonovine tartrate are the most widely used oxytocics. A partially synthetic dihydroergotoxine finds limited use as a peripheral vasodilator.

Ergotamine. Ergotamine was discovered by A. Stoll (2) in 1918, having been isolated from ergot of Central European origin. It was the first pure alkaloid isolated from ergot. In its manufacture the crude drug is intimately mixed with an acid reagent such as aluminum sulfate and is extracted with benzene. This effects a defatting of the drug with little loss of active alkaloid. The drug, covered with benzene, is made alkaline with gaseous ammonia, and the ergotamine is extracted into the benzene. Concentration of the extract in vacuo at a relatively low temperature yields an amorphous residue from which the base can be crystallized from aqueous acetone. Ergotamine tartrate is readily produced by mixing the calculated amounts of base and acid in boiling ethanol.

It has been the author's experience that the above method works well when ergotamine is either the only or the chief peptide alkaloid present in the crude drug. It is of little value when ergotamine is present with like quantities of other peptide alkaloids. Consequently a procedure based on the formation of the phthalate salt was developed (3-5). It eliminated the acidifying process with its subsequent difficult alkalizing step and can presumably be used in the extraction of any ergotamine-containing ergot.

Ergonovine. This alkaloid was isolated simultaneously by four groups of investigators—as ergometrine by Dudley and Moir (6), as ergotocin by Kharasch and Legault (7), as ergobasine by Stoll and Burckhardt (8) and as ergostetrine by Thompson (9). The name adopted by the USP is ergonovine. A number of patents concerning its isolation and preparation of its salts have been issued (10,11).



ergonovine

A practical method for the isolation of ergonovine from foreign ergot and for preparation of the maleate salt was developed by Stuart (12). Unground ergot is first defatted and then extracted with ammoniacal alcohol. The alcoholic extract is concentrated to a low volume, water is added, and the alcohol is removed by vacuum distillation. The water-insoluble material is filtered off, the filtrate is made alkaline to pH 8.5-9.0 with ammonium hydroxide, and the mixture is extracted to exhaustion with ethylene dichloride. This extract yields crude amorphous ergonovine base. Dissolving the base in a small volume of ethanol and adding a solution of maleic acid in a large excess of ether produces crude amorphous ergonovine maleate. Crystallization from methanol-ether and recrystallization from methanol affords a finished product.

While the above process was designed for working with foreign ergot, it is not capable of producing a satisfactory product from domestic ergot, being incapable of coping with pigment and minor water-soluble alkaloidal impurities which carry through into the product. These difficulties were remedied by the following process devised by the author (13): The crude amorphous maleate is further purified by extracting into water, any water-insoluble material being discarded. Extraction with ethylene dichloride at pH 4 removes pigment and three unidentified water-soluble alkaloids of the ergonovine type. Extraction of the alkalized aqueous phase with ethylene

dichloride yields the crude base which can be converted to the maleate as in the Stuart process.

When assayed colorimetrically, domestic ergot is found to contain the equivalent amount of total alkaloids found in Spanish ergot, but only approximately one-half the amount of water-soluble alkaloids calculated as ergonovine—total alkaloids, 2.80 vs 2.81 mg/kg; water-soluble alkaloids, 0.231 vs 0.403 mg/kg.

In 1937, Stoll and Hofmann (14) succeeded in preparing partially synthetic ergonovine by chemical reactions with lysergic acid derived from natural sources. A patent was subsequently issued for the preparation of methylergonovine (15). The method involves condensing isolysergic acid azide with *d*-2-amino-1-butanol. Transposition of the resulting isolysergic derivative to the corresponding lysergic acid derivative is effected by treatment with either acids or alkalies. The mixture of *d*-lysergic acid- and *d*-isolysergic acid-*d*-1-hydroxy-2-butylamide is separated through the chloroform complex. Recrystallization from benzene yields the pure methylergonovine. The use of mononuclear diaroylated tartaric acids (16) has been successfully applied to the separation of the mixtures resulting from the partial synthesis of ergonovine and methylergonovine, the salts being easily separated by fractional crystallization. A serious drawback of this partial synthesis lies in the isomerization and racemization of the lysergic acid group during treatment with hydrazine.

Two other partial syntheses (17,18), each based on the formation of mixed anhydrides, utilize lysergic acid per se of natural origin. Lysergic acid was first obtained by the degradation of ergot alkaloids by Jacobs and Craig (19). A modification of this method involving the cleavage of the crude amorphous total peptide alkaloids and the subsequent preferential adsorption of isolysergic acid on activated carbon, was developed by the author (20). This *d*-lysergic acid monohydrate is the starting material used in both the Pioch and Garbrecht syntheses.

The Pioch method comprises reacting dry *d*-lysergic acid with trifluoroacetic anhydride at a temperature below 0°C, producing a mixed anhydride of lysergic and trifluoroacetic acids. Ergonovine is produced by room-temperature reaction with *l*(+)-2-amino-1-propanol. Because of the bifunctional nature of the alkanolamine used, the reaction product will contain not only the desired hydroxyamide but also a minor amount of isomeric amino ester. The amount of amino ester produced is normally no greater than 25–30% of the total reaction product. The isomeric mixture can be converted to the desired product by subjection to treatment with alcoholic alkali.

The Garbrecht process involves the formation of a mixed anhydride of lysergic and sulfuric acids, followed by reaction with a suitable nitrogenous base to form the desired amide. The mixed anhydride is formed by reacting the lithium salt of *d*-lysergic acid with the sulfur trioxide complex of dimethylformamide. The lysergic acid compound used need not be anhydrous, and the reaction may be performed at ambient room temperature. A salt of lysergic acid is better to use as a starting material than the free acid because of the greater yields that are obtained. The use of the sulfur trioxide complex moderates the course of the reaction, thereby reducing the possibility of the formation of undesirable by-products.

The desired amide is produced by simply mixing the anhydride with the nitrogenous base, *l*(+)-2-amino-1-propanol. The reaction product consists solely of the desired amide, containing no undesired isomeric ester.

Dihydroergotoxine. In 1943, Stoll and Hofmann (21) were able to demonstrate that the amorphous ergotoxine of Barger and Carr (22) and Kraft (23), first crystallized by Smith and Timmis (24), was not a single entity but consisted of three alkaloids,

ergocristine, ergocornine, and ergokryptine. They succeeded in hydrogenating these naturally occurring alkaloids (25), and it was determined that the dihydro compounds have no action on the uterus, possessing only sympathicolytic activity.

The reaction is carried out by subjecting the alkaloids to treatment with hydrogen under pressure in the presence of nickel or palladium and dioxane or dioxane-water. The transposition from the lysergic acid series to the isolysergic acid series does not occur.

The synthesis of dihydrolysergic acid by Uhle and Jacobs represents the first major accomplishment in the synthetic studies (26). The total synthesis of lysergic acid and ergonovine has been achieved by the classical efforts of Kornfeld, Fornefeld, Kline et al. (27). It involves a fifteen-stage sequence, starting with 3- β -carboxyethyl-indole and converting to 1-benzoyl-5-keto-1,2,2a,3,4,5-hexahydrobenz[*cd*]indole, which in turn is transformed to 9-keto-7-methyl-4,5,5a,6,6a,7,8,9-octahydroindolo[4,3-*fe*]quinoline and then to lysergic acid. While the method is presently not commercially practical, it has made possible the pharmacological investigation of a variety of intermediates closely related to the active ergot alkaloids.

A host of investigators have attempted to produce ergot alkaloids biosynthetically, and it was only recently that an apparently successful method was devised. Arcamone et al. (28) have reported the biosynthesis of a number of lysergic acid derivatives in submerged cultures of *Claviceps paspali* Stevens and Hall, a fungus parasitizing *Paspalum distichum* L. in Italy.

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Ipecac Alkaloids

Ipecac was known to the natives of South America who used the drug to treat diarrhea. It was introduced into Europe from Brazil in 1658, but its use against dysentery was not recommended until 1829 by Bardsley (1).

Two kinds of ipecac (*Rubiaceae*) are important in commerce. The Rio or Brazilian ipecac consists of the dried rhizomes and roots of the indigenous *Uragoga ipecacuanha* (Brot.) Baill. (*Cephaelis ipecacuanha* (Brot.) A. Rich.). When cultivated in India, the Indies, or Malaya, it is known as Jahore ipecac. The Cartagena, Nicaragua, or Panama ipecac is obtained from *Uragoga acuminata* (Benth.) Kuntze. The Rio variety usually contains slightly more than 2% total alkaloids, 60–70% of which consists of emetine and 25% of cephaeline. The Cartagena variety usually contains 2.5% or more total alkaloids, but the cephaeline content is greater than in the Rio type.

Emetine is the principal alkaloid of ipecac and it is usually supplied as the dihydrochloride. It finds its chief use in the treatment of acute amebiasis, amebic hepatitis, and amebic abscesses. It is lethal to the motile forms of *Endamoeba histolytica*, but is not too effective against the cyst form. While it is also an emetic and expectorant, the galenical forms of the drug are more suitable for these purposes. Whereas the preferred route of emetine administration is subcutaneous, its combination with bismuth iodide can be given orally.

Cephaeline (desmethylemetine) is similar in action to emetine, but it is more toxic and irritant. It is not used medicinally, but is converted to emetine by *O*-methylation.

Emetine. This alkaloid was first obtained in the amorphous form by Pelletier and Magendie (2) and was first prepared in the pure state, free of cephaeline, by Paul and Cownley (3). Its commercial preparation presents no unusual problems and general techniques are employed. Care must be exercised, however, in handling the crude drug and the dried products, as they are capable of causing severe conjunctivitis, epidermal inflammation, and asthma.

The following method demonstrates the manufacture of emetine and is easily reproducible. The powdered root is extracted with hot 50% methanol or 70% ethanol. After the solvent has been removed, an equal volume of water is added to the resulting syrup. The aqueous solution is made alkaline with ammonia, and the alkaloids are extracted therefrom with a water-immiscible organic solvent. The organic extract is treated with a dilute aqueous solution of potassium hydroxide to remove the cephaeline and other phenolic bases, and this extract is kept for the recovery of the cephaeline and its eventual conversion to emetine by methylation. The nonphenolic bases are extracted from the organic phase with dilute sulfuric acid, and the emetine is recovered as the hydrobromide or hydriodide from the neutralized solution. The free base is liberated and converted to the hydrochloride.

The *O*-methylation of cephaeline can be achieved by the use of a number of methylating agents. The two agents of choice are phenyltrimethylammonium hydroxide and nitrosomethylurethane. Cephaeline can be *O*-methylated without effecting *N*-methylation by heating with phenyltrimethylammonium hydroxide at 130–140°. The reaction mixture is acidified slightly and the resulting dimethylaniline is extracted with petroleum ether. Alkalinization with fixed alkali and extraction with ether yield emetine in 96% yield (4).

Methylation can also be effected in good yield by nitrosomethylurethane (5).

The total synthesis of emetine has been reported by Evstigneeva et al. (6); a synthesis from hexahydrogallic acid has been reported by Burgstahler and Bithos (7).

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Lobelia Alkaloids

The plant *Lobelia inflata* L. (*Lobeliaceae*) contains at least fourteen alkaloids, but only one of these is of interest, namely the monoacidic, tertiary base, *l*-lobeline. While lobelia and its galenical preparations are obsolete in modern therapeutics, lobeline sulfate and hydrochloride are widely used in controlling symptoms in persons attempting withdrawal from the tobacco habit. A cross tolerance between it and nicotine makes this control possible. It is usually administered orally in capsules or as a chewing gum. The commercial sulfate utilized for this purpose is usually that of a mixture of the total alkaloids of lobelia.

The methods of isolation of the lobelia alkaloids and the elucidation of their structures are due primarily to the work of Wieland and his students who, in the period of 1921–1939, published a series of papers dealing with these matters (1,2). Patented methods of isolating and manufacturing the lobelia alkaloids (3) utilize the ability of lobelanine hydrochloride (the corresponding diketo alkaloid and the second most abundant) to crystallize from dilute hydrochloric acid while the lobeline hydrochloride is extracted therefrom with chloroform. Lobelanidine, the corresponding dihydroxy alkaloid, which accompanies lobeline and lobelanine, is recovered from the mother liquors.

The final yield of *l*-lobeline hydrochloride is augmented by converting the secondary bases to the parent alkaloid. This in essence involves a reduction to lobelanidine, a partial oxidation to *d,l*-lobeline, and a subsequent resolution to the *l*-lobeline. Another method involves oxidation of the secondary bases to lobelanine, which is then partially reduced.

Synthesis of members of the lobeline group, and consequently that of *l*-lobeline, has been effected by Wieland and Drishaus (4), Scheuing and Winterhalder (5), and

Schöpf and Lehmann (6). In the first method the synthesis of lobelanidine was effected by condensing ethyl glutarate with acetophenone in the presence of sodamide. The resulting 1,7-dibenzoyl-2,6-heptadione was treated with ammonia to yield the piperidine derivative. Catalytic hydrogenation over platinum oxide yields a mixture of unsaturated glycols. Reduction of the β -diene with aluminum amalgam produces norlobelanidine, which can be methylated to yield lobelanidine.

The second method involves treating 2,6-distyrylpyridine tetrabromide with alcoholic potassium hydroxide to yield 2,6-diphenethinylpyridine. Hydration with 50% sulfuric acid gives 2,6-diphenacylpyridine, which can be reduced to the corresponding disecundary alcohol and then to norlobelanidine by hydrogenation in methanol over a platinum oxide-barium sulfate catalyst. A better yield of lobelanidine is obtained when 2,6-diphenacylpyridine methyl-*p*-toluenesulfonate is catalytically reduced.

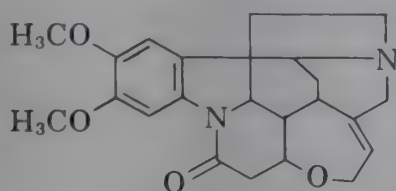
The third synthesis is one carried out under so-called physiological conditions, wherein a mixture of glutaric dialdehyde, methylamine hydrochloride, and benzoyl-acetic acid is allowed to stand for 8 hours at 25°C in a solution buffered at pH 4, resulting in a 90% yield of lobelanine. The pH range at which good yields are realized is very narrow.

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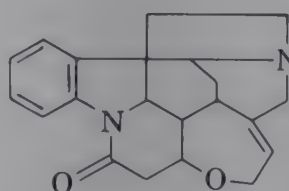
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Nux Vomica Alkaloids

Strychnine is the most important alkaloid obtained from the dried ripe seed of *Strychnos Nux-vomica* L., *S. ignatii* Berg., and other species of *strychnos* (*Loganiaceae*). Both of the first two contain 2–3% of total alkaloids, of which approximately one-half in the first drug and two-thirds in the second drug is strychnine, the balance consisting chiefly of brucine. Strychnine was first isolated from *S. ignatii* in 1818 by Pelletier and Caventou, who also isolated brucine in 1819 (1).



brucine



strychnine

Strychnine is usually available as the base, nitrate, phosphate, and sulfate salts. It is one of our most powerful central nervous system stimulants and has been widely used in therapy. The galenical forms find use chiefly as bitter tonics. The only rational use of strychnine is as an antidote for poisoning by or accidental overdosage

of central nervous system depressants, primarily the barbiturates. Its chief non-medicinal use is as a vermin killer.

Brucine resembles strychnine in action and is less toxic. It is seldom used in therapy.

Strychnine. The extraction of the drug for strychnine is conducted in a manner general for many alkaloids. The ground drug is alkalized with sodium carbonate and is extracted with a water-immiscible organic solvent at an elevated temperature. Toluene is usually the solvent of choice. The alkaloids are extracted from the concentrated extract with dilute sulfuric acid. Careful neutralization of the aqueous phase precipitates the amorphous alkaloids. Crystallization from either alcohol or methanol produces a semipure strychnine, the bulk of the brucine remaining in the mother liquors. The strychnine can be freed of the last traces of brucine by crystallization as the sulfate, and then, finally, by recovery as the crystalline base from ammoniacal alcohol or methanol. A U.S. patent has been issued for the isolation of strychnine (2). The total synthesis of strychnine has been achieved recently through the masterful efforts of Woodward and co-workers (3,4).

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Opium Alkaloids

Opium is the air-dried, milky exudation from incised, unripe capsules of *Papaver somniferum* L. or *P. album* Mill. (*Papaveraceae*). Until well into the nineteenth century, the only opium preparations used were the galenicals. Morphine was isolated in 1803 by the German pharmacist Sertürner, but this first isolation of an alkaloid from a plant went unnoticed until his later publication in 1816. The discovery of other opium alkaloids soon followed, and the use of pure alkaloids rather than crude preparations soon spread throughout the medical field.

P. somniferum is indigenous to Asia Minor, and Arabian physicians were well-versed in its use. The drug was introduced into the Orient by Arabian traders. The spread of the opium habit throughout China did not occur until the latter part of the eighteenth century. This was accomplished first by the Portuguese and then by the English to exploit the natives. Opium traffic and subsequent addiction proved to be a useful tool as a source of revenue and means of conquest.

The principal opium-exporting countries are Turkey, Yugoslavia, Iran, and India. The Turkish and Yugoslav products are nearly alike in their physical properties, as are the Iranian and Indian products. The latter are darker and have a different odor and consistency. The former contain higher percentages of morphine, while the latter are richer in codeine and papaverine.

Opium owes its value as an analgesic and narcotic to the more than twenty-five narcotic alkaloids present, but it owes its chief pharmacological effects to its major alkaloid, morphine. Powdered opium is available, the average adult oral dose being 0.06 g. This is equivalent to 6 mg of morphine. The tincture is more commonly

used for cases of diarrhea and dysentery. Opium produces sedation and sleep, and a number of preparations are used in the control of cough and dyspnea. Only three of the alkaloids are presently used widely for clinical purposes, ie, morphine,, codeine, and papaverine.

Morphine. Derosne (1) was the first to isolate a crystalline material from opium. It was probably a mixture of morphine and narcotine, and he apparently failed to recognize the basic character of this material. Séguin described the isolation and properties of morphine, suggesting its basic characteristics, in a report to the Academy of Sciences in 1804. However, this paper was not published until 1814 (2). Sertürner described the isolation of the pure base in 1805 (3), but this paper on the subject went unnoticed. It was not until his later papers were published (4) that intense interest was aroused. Other investigators readily duplicated his work, and the isolation of other opium alkaloids followed shortly.

Most processes used to isolate morphine are considered to be based on the method of Gregory (5), with improvements developed by Anderson (6). Detailed manufacturing procedures have been described by Schwyzer (7), Barbier (8), Kanewskaja (9), and Chemnitius (10). In nearly all of the processes in use morphine and most of the other opium alkaloids are extracted with either water or slightly acidified water. If water alone is used as a solvent, the solution is concentrated, mixed with alcohol, and made strongly alkaline with ammonia. Morphine precipitates, while most of the other alkaloids remain in solution. The crude morphine is purified by repeated crystallization as the sulfate or hydrochloride. If slightly acidified water is used as a solvent, the solution is concentrated and neutralized and is treated with a strong solution of calcium chloride. This serves to precipitate the calcium salts of meconic, lactic, and sulfuric acids. The filtrate is then further concentrated, and crude morphine chloride crystallizes. This is then further purified by precipitation with ammonia, the codeine which is usually present remaining in solution. Final purification is effected by recrystallization as either the sulfate or hydrochloride.

The use of ion-exchange resins for the isolation of morphine presents promising commercial possibilities. One method (11) involves extraction of the poppy capsules and stems (straw) with ammoniacal water-saturated isobutyl alcohol. The extract is then passed continuously through a cation-exchange resin bed, and then through an anion-exchange resin bed. Either Zeo-Karb H or Duolite C-10 is capable of adsorbing the base from the extract, the former having a 55% greater adsorptive capacity for morphine than the latter. The effluent is treated with ammonia and the cycle is repeated. The alkaline eluates are neutralized and the crude alkaloids are precipitated.

The total synthesis of morphine has been achieved by Gates and Tschudi (12). A U.S. patent has been issued for the preparation of various phenanthrene compounds, particularly for those intermediates useful in the synthesis of codeine. Since codeine can be converted to morphine, this method represents one capable of synthetically producing both of these alkaloids (13).

The major use of morphine is for the relief of severe pain. Morphine is available as the free base but it is usually prescribed as a water-soluble salt. The sulfate and the hydrochloride are the two salts most commonly used.

Codeine. This alkaloid is the methyl ether of morphine. It was first isolated in 1832 by Robiquet (14,15), as an impurity accompanying morphine in the course of extraction by the Gregory process. It occurs in opium from 0.7–2.5% depending on the source. While some codeine is extracted from opium directly, this source is not

sufficient to supply the demand. A number of methods have been described for the separation of codeine and morphine (9). The bulk of the codeine used today is supplied by the methylation of morphine. The methylating agent generally used is trimethylphenylammonium sulfate or chloride (16), which is prepared by heating dimethylaniline with dimethylsulfate or methyl chloride in alcohol or toluene under pressure. The morphine is dissolved in dry ethanolic potassium hydroxide solution, the methylating agent is added and the mixture is heated to 130°C. The reaction mixture is cooled, diluted with water, and acidified with sulfuric acid. The dimethylaniline formed is separated and the ethanol is removed by distillation. Treatment with sodium hydroxide solution serves to precipitate the codeine, while dissolving any unreacted morphine. The codeine can then be purified by recrystallization or as the sulfate.

Therapeutically, codeine is considered as a weakened morphine which fails to produce proportionately greater narcotic effects with increased dosage. Average doses are sedative and analgesic and serve to depress the excitability of the cough reflex. It is available as the free base and as water-soluble salts. The salts usually employed are the sulfate and the phosphate, the latter being more soluble.

Papaverine. This alkaloid is present in opium to the extent of 0.8–1.0%. It was first discovered in the morphine mother liquors by Merck (17). It is usually accompanied by narcotine, but the two can be separated by crystallizing papaverine as the acid oxalate (18,19). The base can be further purified by recrystallization from ethanol.

The bulk of the papaverine used today is produced synthetically. It was first synthesized from veratrol and homoveratric acid in 1909 by Pictet and Gams (20,21). A number of other synthetic routes have been evolved, and today the bulk of the world's needs of papaverine is met by preparation from either vanillin or guaiacol. One method (22,23) involves condensing veratraldehyde with nitromethane. The styrene derivative formed is treated with methanol, and the resulting product is reduced with sodium amalgam. The methoxyamine is condensed with veratroyl chloride, yielding the β -methoxy amide. Treatment with phosphorus pentoxide or phosphoryl chloride gives papaverine.

Pictet and Finkelstein (24) improved the original synthesis of Pictet and Gams by condensing β -(3,4-dimethoxyphenyl)ethylamine with homoveratroyl chloride. Cyclization of the resultant amide with phosphoryl chloride gives dihydropapaverine. Späth and Burger (25) demonstrated that reduction of the latter could be achieved by heating with palladized asbestos at 200°C to give the alkaloid in good yield.

A third important synthesis was described independently by Wahl (26) and Galat (27). Condensation of veratraldehyde with hippuric acid in the presence of acetic anhydride and sodium acetate yields an azlactone, which is hydrolyzed with sodium carbonate to yield veratrylidenehippuric acid. This undergoes autocondensation when heated with aqueous ammonia, and the resulting product is esterified and cyclized with phosphoryl chloride, giving 3-carbethoxy-3,4-dihydropapaverine. Hydrolysis, decarboxylation, and reduction yield papaverine.

In all probability more than 95% of the papaverine used is supplied by the three methods just described. Two other interesting schemes have been described by Buck as well as Young and Robinson (28) and by Späth and Berger (29).

Papaverine is an antispasmodic for smooth muscle. It finds use in the treatment of peripheral arterial embolism, as well as pulmonary embolism. It has been employed in the case of severe cardiac pain due to coronary occlusion. It is not generally as

useful or reliable as nitroglycerin in the treatment of angina pectoris. Unlike the other useful opium alkaloids, papaverine is not a narcotic. It is usually supplied as the hydrochloride. The drug can be administered orally, intramuscularly, or intravenously.

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Pilocarpus Alkaloids

The name "jaborandi" is applied to a number of closely related South American plants. The natives chewed the leaves to produce salivation. Dr. Coutinhou, a Brazilian physician, first demonstrated that an extract of the leaves caused marked sweating and he was responsible for introducing the drug into Europe in 1874. In 1876, Weber described its action on the pupil of the eye, as well as on the sweat and salivary glands (1).

The botanical sources of the early samples were *Pilocarpus jaborandi* Holmes (*Rutaceae*) and *P. pennatifolius* Lem. These were later replaced by *P. microphyllus* Stapf, and this is the current major source.

Pilocarpine is the major alkaloid in this drug, and it was isolated independently by Gerrard (2) and by Hardy (3). It is presently available as either the hydrochloride or the nitrate. The former use as a diaphoretic is now considered obsolete. The

chief use of the drug is to produce miosis and in this respect pilocarpine is useful in overcoming the mydriasis produced by atropine and in glaucomatous conditions.

Pilocarpine. It has been recommended that only new and thoroughly dried leaves be used in the manufacturing of pilocarpine (4). The total alkaloid content of the crude drug decreases by as much as 50% during storage over a period of one year, even under proper conditions of storage. Hot and humid conditions accelerate the decomposition.

While several manufacturing processes have been described in the literature (4,5), the one designed by Stoll (6) appears to have the most merits. The alkaloids are bound in the drug as salts by the addition of acidic reagents prior to defatting with benzene. The leaves are then made alkaline and the total alkaloids are extracted with benzene. Pilocarpine is most frequently contaminated with its stereoisomer isopilocarpine. The latter is qualitatively similar to pilocarpine in its physiological effects, but is less active. The pilocarpine is purified via the nitrate, the salt being prepared by the judicious addition of nitric acid to a chilled alcoholic solution of the base. Several recrystallizations of the nitrate from methanol may be required to remove contaminating alkaloids.

The hydrochloride may be prepared from either the base or the crude nitrate but, because of its hygroscopicity, it is less convenient to handle.

The synthesis of pilocarpine was first achieved by Preobrazhenskiĭ and co-workers (7), and they subsequently proposed a method for commercial synthesis (8). A shortened synthesis is the subject of a U.S.S.R. patent (9). An independent synthesis has also been proposed by Dey (10).

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Rauwolfia Alkaloids

The *Index Kewensis* lists more than 175 proposed species of the genus *rauwolfia* (fam. *Apocynaceae*) (1), but according to Woodson (2), an authority on this genus, only about half of these will eventually be found to be valid. The crude drug was reportedly used in Indian medicine as a febrifuge, a remedy for snake bite, and a cure for dysentery (3). Hypotensive activity of an extract from *R. serpentina* Benth. was reported in 1933 (4). For a number of years prior to 1952 various species of the genus received much more attention from pharmacologists than from chemists. This

situation changed dramatically with the isolation of a hypotensive and neurosedative principle, reserpine, by Müller, Schlittler and Bein (5). Two other similarly acting alkaloids were isolated later, ie, rescinnamine and deserpidine (canescine, recanescine). All three are presently utilized in medicine. In addition to these pure alkaloidal components, the powdered root and alcoholic extracts thereof are available and are widely used.

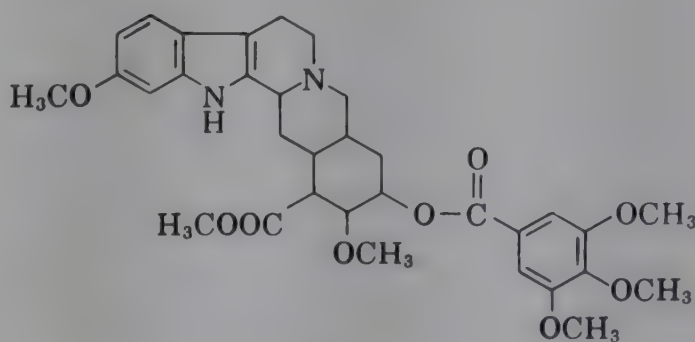
Reserpine. Five species of *rauwolfia* have been used in the commercial production of reserpine, viz, *R. serpentina* (5), *R. canescens* (6), *R. micrantha* (7), *R. tetraphylla* (*hirsuta* or *heterophylla*) (8), and *R. vomitoria* (9). The methods by which reserpine was first isolated from each of these species, respectively, are described in the references cited following each species.

India was the major exporter of *R. serpentina* and, in April 1954, the Indian government invoked the now famous embargo on that commodity. As has happened in the past, the search for other reserpine-yielding species was intensified, and it was soon found that the African *R. vomitoria* Afz. yielded greater quantities of the alkaloid thereby relegating *R. serpentina* to a secondary choice.

Two U.S. patents have been issued to Schlittler and Müller for crystalline reserpine and its salts and for processes of producing them (10). One method involves extracting the ground root with methanol or methanol-chloroform mixtures and concentrating the extract to dryness in vacuo. The residue is extracted with water to remove the water-soluble impurities, dilute hydrochloric acid to remove strongly basic impurities and, finally, petroleum ether to remove the fat-solubles. An ethanolic extract of the remaining residue is subjected to countercurrent distribution and column chromatography on alumina.

A second method utilizes dilute acetic acid as the extracting solvent. The acid extract is then extracted with chloroform, and the chloroform-solubles are chromatographed on alumina. A third method utilizes the formation of the insoluble hydrochloride to effect purification.

In an alternate procedure (11) the crude drug is intimately mixed with 2% tartaric acid, defatted and then extracted with benzene. The presence of the tartaric acid serves to bind the stronger bases in the drug, affording an initial separation of the weak and strong bases during extraction. The concentrated benzene extract is vacuum-steam-distilled with 2% tartaric acid and the reserpine is extracted from the aqueous phase with ethylene dichloride at a pH of 3.4–3.6. The addition of methanol to this extract produces crystalline reserpine.



reserpine

The complete structure of reserpine emerged from the elegant work of the Ciba group (12), and shortly thereafter the final proof of structure was demonstrated by the

synthesis of Woodward and his co-workers (13). This may be considered a seven-stage synthesis starting with the acylated racemic lactam 18 β -acetoxy-11,17 α -dimethoxy-3-oxo-16 β -methoxycarbonyl-2,3-*seco*-20 α -yohimbane, and finally producing reserpine by the esterification of methyl reserpate with trimethoxybenzoyl chloride.

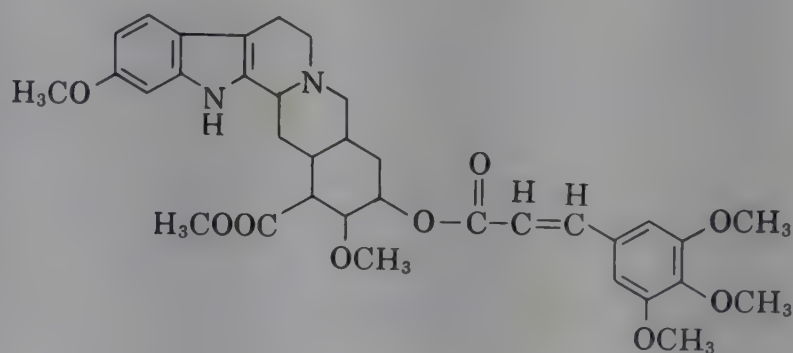
A greatly simplified and more efficient synthesis, that appears to be commercially feasible, has been patented by Joly and Bucourt (14). It applies not only to reserpine but also to rescinnamine and deserpidine. The process eliminates at least three steps of the Woodward synthesis. Simply stated, reserpine can be prepared from dextro-rotatory 18 β -hydroxy-11,17 α -dimethoxy-16 β -methoxycarbonyl-3-oxo-2,3-*seco*-20 α -yohimbane by esterification with 3,4,5-trimethoxybenzoyl chloride, followed by cyclization to 3,4-dehydroreserpine and subsequent reduction.

Rescinnamine can be prepared from the same starting material by esterification with 3,4,5-trimethoxycinnamoyl chloride, cyclization with phosphorus oxychloride (yielding levorotatory 3,4-dehydrorescinnamine), and subsequent reduction with zinc and acetic acid.

Deserpidine can be similarly synthesized by esterification of dextrorotatory 18 β -hydroxy-17 α -methoxy-16 β -methoxycarbonyl-3-oxo-2,3-*seco*-20 α -yohimbane with trimethoxybenzoyl chloride, cyclization with phosphorus oxychloride and reduction of the resulting levorotatory 3,4-dehydrodeserpidine with zinc and acetic acid.

A synthetic analog of reserpine, carbethoxysyringoyl methylreserpate, enjoys wide use and is reported to produce the cardiovascular effects of the rauwolfia alkaloids with fewer of the side effects.

Rescinnamine. This base, the 3,4,5-trimethoxycinnamic acid ester of methylreserpate, was isolated by Klohs and co-workers (15). It is reported to produce essentially the same pharmacological effects as does reserpine. It was obtained by subjecting the benzene-soluble portion of the methanolic mother liquors from reserpine to column separation on Merck acid-washed alumina.



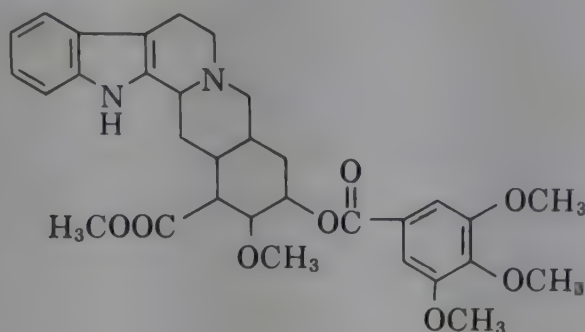
rescinnamine

This same alkaloid was independently isolated by Haack et al. (16) and was given the name "reserpinine." Several U.S. patents have been granted for its isolation and purification (17-19). The first is based on isolation of the alkaloid from the reserpine methanolic mother liquors, as the readily crystallizable benzene complex. Rescinnamine recovered by this process is stated to be generally 70-90% pure. The second takes advantage of the formation of insoluble naphthoates. The third utilizes Amberlite IRC-50, a cation-exchange resin, and column chromatography on acid-washed alumina.

Dihydrorescinnamine, wherein the double bond of the trimethoxycinnamic acid moiety of rescinnamine has been saturated, has been patented (20). It is stated

to be less toxic than either reserpine or rescinnamine, possessing the same or slightly less sedative activity while being a more potent hypotensive agent.

Deserpidine. This alkaloid, 11-desmethoxyreserpine, was simultaneously isolated by four groups of investigators. Schlittler and co-workers (21) reported this base as a minor constituent in a number of *rauwolfia* species. Stoll and Hofmann (22) isolated this alkaloid, which they called "canescine," from the roots of *R. canescens* L., as did Klohs et al. (23). Neuss and colleagues (24) also isolated this alkaloid as "re-canescine" from the same source. It is reported to have biological activity similar to reserpine.



deserpidine

Deserpidine is usually isolated from the methanol mother liquors of reserpine by column chromatography on alumina. A novel process, on which a U.S. patent has been granted (25), utilizes formation of the thiocyanate salt. When reserpine is present in the starting material, it is removed as the insoluble thiocyanate, while the deserpidine remains in the mother liquor.

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The Solanaceous Alkaloids

The alkaloids atropine, hyoscyamine, and scopolamine are often referred to as "solanaceous alkaloids," but they are not the only type of alkaloid found in the botanical family *Solanaceae*. They are also called "mydriatic alkaloids," but other alkaloids also possess mydriatic action.

The most characteristic physiological property of these alkaloids is their ability to dilate the pupil of the eye (mydriatic). Atropine, *A. belladonna*, and its galenicals are frequently used alone, or in combination with phenobarbital, for antispasmodic effects on the bowel, as are hyoscyamine, *Hysoscyamus*, and its galenicals. Scopolamine, because of its powerful sedative and tranquilizing depressant effect on the central nervous system, is widely used to combat nausea. Atropine is usually employed in the form of the sulfate, hyoscyamine as the hydrochloride, and scopolamine usually as either the hydrobromide or methylbromide.

Atropine (*dl*-Hyoscyamine) and *l*-Hyoscyamine. Atropine, the optically inactive, racemic form of *l*-hyoscyamine, was isolated by Mein (1) in 1831. It does not normally occur in more than trace amounts in solanaceous plants, and its isolation is usually the result of partial racemization during extraction of the *l*-hyoscyamine present; this process can be completed under such diverse conditions as treatment with dilute alkali in cold alcoholic solution (2,3), treatment with ammonia (2), heating in vacuo (2), or boiling in chloroform (4,5).

l-Hyoscyamine is the most commonly found alkaloid in solanaceous plants, and it is usually associated with varying amounts of *l*-scopolamine. It was first isolated from henbane (*Hyoscyamus niger* L.) by Geiger (6). The principal sources of *l*-hyoscyamine are *Hyoscyamus muticus* L., *H. niger* L., *Datura stramonium* L., and *Atropa belladonna* L. Because of its high alkaloid content, *H. muticus* is the preferred source for the manufacture of atropine, and *D. stramonium* is the second choice. The ground drug is alkalized with an aqueous solution of sodium carbonate and is extracted with benzene. The alkaloids are then extracted from the concentrated benzene extract with dilute acetic acid, and the resulting extract is treated with ether to remove coloring matter. The bases are precipitated from the aqueous phase by making the latter alkaline with sodium carbonate. The amorphous bases are crystallized from acetone and consist of a mixture of atropine and *l*-hyoscyamine. The isolated crystals are dissolved in alcohol, sodium hydroxide solution is added, and the mixture is allowed to stand until the racemization is complete. The crude atropine is then recrystallized from acetone.

Atropine sulfate is prepared by the judicious addition of methanolic sulfuric acid to a chilled methanolic solution of atropine, and the entire operation is carried out in the cold (7).

***l*-Scopolamine.** The *l*-hyoscyamine isolated by Ladenburg (8) in 1881 from *l*-hyoscyamine mother liquors obtained from *H. muticus* was shown to be identical with the scopolamine later isolated by Schmidt from *Scopola atropoides* Bercht. and Presl (9).

l-Scopolamine is presently obtained indirectly from the mother liquors resulting from the crystallization of hyoscyamine; it can also be obtained directly from the leaves of *Datura metel* L. or *D. meteloides* L., in which plants it occurs as the major alkaloid. Select species of *duboisia* may prove to be even better primary sources (10–12). A process for the manufacture of this alkaloid has been described by Chemnitius (13). The ground drug, alkalinized with 10% aqueous potassium hydroxide, is extracted with ether. The base is converted to the hydrobromide, and this salt is crystallized from an acetone–ethanol mixture. A method for the recovery of *l*-scopolamine from racemized base has been described by Shchukina and co-workers (14).

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Veratrum Alkaloids

The veratrum group (*Liliaceae*) has been used empirically for centuries in the treatment of fevers, as cardiac tonics, emetics, and local counterirritants in neuralgia, as crow poisons, and as insecticides (1,2). In the United States, the use of veratrum preparations in the treatment of hypertension goes back at least a hundred years (3). Early treatment with crude alkaloidal extracts produced erratic results and soon fell into disrepute. The chief difficulty lay in the fact that the dosage range between hypotensive and emetic effects was a narrow one. Interest was renewed in the late 1930s with the advent of purified alkaloidal preparations which were responsible for the hypotensive activity.

More than forty alkaloids have been isolated from various species of veratrum, schoenocaulon, and zygadenus (4), but only the ester alkaloid, protoveratrine, has found any widespread use as a hypotensive agent (5–7). A powdered extract of *Veratrum viride* Aiton alkaloids is available, as is a biologically standardized preparation of the whole powdered drug; this latter is enjoying the widest use of any of the veratrum preparations.

Protoveratrine. The so-called protoveratrine of commerce is actually a mixture of two alkaloids, protoveratrines A and B, in varying proportions. This mixture was first isolated by Salzberger from *Veratrum album* L. (8) and was reexamined by Poethke (9) and Craig and Jacobs (10). In the procedure used by the latter, roots of *V. album*

were extracted with ammoniacal benzene, and the alkaloids were extracted therefrom with dilute acetic acid. The aqueous extract was made alkaline and extracted with benzene. The residue remaining upon evaporation of the benzene was then extracted with ether. The ether-insoluble residue yielded crude amorphous protoveratrine. Repeated crystallization from chloroform-ether mixtures yielded crystalline protoveratrine, the quality of which varied with different lots.

Several U.S. patents have been issued dealing with the removal of contaminating ether-insoluble alkaloids from crystalline protoveratrine (11). Advantage is taken of the solubility of the contaminants in either acetone or *n* butyl chloride.

Protoveratrines A and B. Countercurrent distribution between chloroform-ethylene dichloride and 2% acetic acid has yielded the two pure entities (12). Both of the resulting pure alkaloids possess hypotensive activity and may be used alone or in combination, or each may be added to the so-called protoveratrine to produce a uniform, reproducible product mixture.

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Vinca Alkaloids

The newest of the alkaloid-containing plants to elicit the interest of phytochemists, pharmacologists, biologists, and clinicians is the pantropical herb or subshrub *Vinca rosea* Linn. (*Catharanthus roseus* G. Don, *Lechnera rosea* Reichb.). While the use of this drug has been reported in Brazil for controlling hemorrhage, in treating scurvy, as a mouthwash for toothache, and for healing and cleaning chronic wounds (1), it was the alleged hypoglycemic action (2,3) of the alkaloid which initiated work independently in two different laboratories, unknown to each other. Recent work by a group of Indian investigators (4) has indicated that the total alkaloids exhibit a limited antibiotic activity and a significant and sustained hypotensive effect.

Although neither group investigating the hypoglycemic activity could substantiate this effect, the Canadian group observed that certain fractions produced a peripheral granulocytopenia and bone marrow depression in rats (5-8) and the Lilly group observed a reproducible effectiveness of certain preparations against the P-1534 type of leukemia in DBA/2 mice (9-12).

Two new alkaloids, vincalkeboblaine (VLB) (as sulfate) and leurosine were subsequently obtained. Both alkaloids possess demonstrable activity against P-1534 leukemia, but leurosine has not been as active or as consistent an inhibitor of this leukemia as has VLB. Consequently, the major portion of the biological studies

and clinical evaluation has been devoted to work with VLB. This alkaloid is reported to be effective against Hodgkin's disease, chorionepithelioma, and breast cancer (13-23). VLB and related chemical compounds are clinically active substances of new chemical composition which provide new and heretofore unknown leads in cancer chemotherapy.

Vincaleukoblastine and Leurosine. Of the twenty-eight alkaloids obtained from this plant (11,24,26,28), only VLB is presently marketed for its oncolytic activity. It was first obtained by Beer (7) from the leaves of *V. rosea* with ethanol containing 10% acetic acid. The residue from this extract was extracted with aqueous 2% hydrochloric acid, and the aqueous phase was adjusted to pH 4.0 and extracted with benzene or chloroform. The aqueous phase was then adjusted to pH 7.0 and extracted with benzene. This benzene solution was chromatographed on Woehlm alumina, Grade IV-V, using the method of gradient elution. Fraction 9 eventually yielded the crystalline sulfate.

The method which the author devised for leurosine (9,11) was found to be readily applicable to VLB and is an example of a production method obtained by a direct scale-up of a designed laboratory procedure. As discussed in the introduction to general methods of extraction, the process consists in separating the alkaloids into those whose tartrates are soluble and those whose tartrates are insoluble in organic solvents. Final purification is achieved by elution chromatography on deactivated alumina, followed by direct crystallization of the base (leurosine) or formation and crystallization of the sulfate (VLB). The extraction scheme is shown in Figure 1.

Leaf drug, pretreated with 2% tartaric acid, is extracted with benzene. The "marc" (exhausted leaves) is discarded. The concentrated benzene extract is vacuum-steam-distilled with 2% tartaric acid, and any insoluble material is discarded. Extraction of the aqueous phase with benzene at pH 3.0 affords the removal of the very weak bases, which are discarded. Extraction of the alkalized aqueous phase with benzene yields the so-called (A) fraction, which contains the leurosine and VLB. This processing is done in conventional equipment.

The chromatographic separation was an actual 120-fold scale-up of the laboratory procedure. The (A) fraction was charged onto three stainless-steel columns (7' × 8") packed with deactivated alumina. A rotameter was used to maintain the same rate of

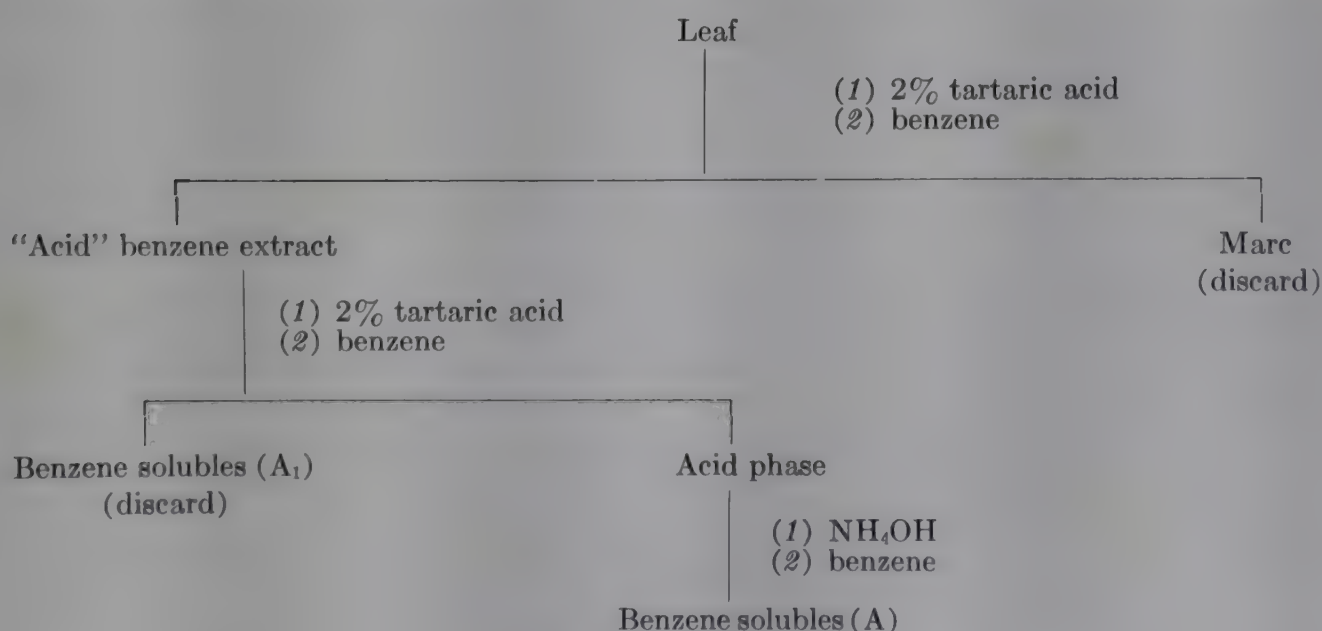


Fig. 1. Extraction scheme.

flow from each column. While the eluate from the three columns was collected separately, the overall operation was considered as one column, eluate combinations being made on the basis of similar solvent mixtures.

These were concentrated in vacuo to bench volumes, and the addition of methanol to certain cuts produced crude crystalline leurosine. Aliquots of these mother liquors and of several of the following cuts were treated for sulfate formation. The use of a specific color test for VLB (25) in the various chromatographic cuts has facilitated their workup. This test is based on the deep rose color produced by an appropriate mixture of acetic anhydride, acetyl chloride, pyridine, and sulfuric acid.

Once located, the appropriate cuts were combined, and VLB sulfate was made in the usual manner and recrystallized from ethanol.

Leurosidine and Leurocristine. It has been recognized that the indefinite prolongations of life observed in the laboratory for DBA/2 mice infected with P-1534 leukemia and treated with certain column fractions was attributable to neither VLB nor leurosine, nor their combination (12). Rechromatography of the chloroform-soluble post-VLB eluate and application of a gradient pH technique to certain anti-leukemia-monitored fractions has yielded these two new active dimeric alkaloids, leurosidine and leurocristine (26).

The gradient pH technique used in obtaining these alkaloids involved dissolving the crude selected fraction in benzene and then extracting into 0.1M citric acid. The pH of the aqueous phase was raised in approximately one-half unit increments from 2.8 to 7.5, benzene extractions being made at each level. Leurocristine and its sulfate were obtained at pH levels of 4.9, 5.4, and 5.9, while leurosidine was obtained from 5.4, 5.9, and 6.4. In a number of cases leurosidine was isolated from methanol as a first-crop crystal while leurocristine was obtained as the second crop from the concentrated mother liquor.

Both of these alkaloids are more active than either VLB or leurosine, and both possess a broader tumor spectrum (27). Preliminary clinical studies with leurocristine suggest a striking percentage of complete hematological remissions in acute lymphocytic leukemia and responses in a spectrum of solid tumors (29-36).

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ALKANOLAMINES

The alkanolamines are amino alcohols; they can be considered as derivatives of ammonia in which at least one hydrogen is replaced by a hydroxyalkyl radical. Two groups of alkanolamines have attained commercial importance. These groups are discussed separately since their methods of manufacture are widely different.

Alkanolamines from olefin oxides and ammonia.....	810
Bibliography.....	823
Alkanolamines from nitro alcohols.....	824
Bibliography.....	831

ALKANOLAMINES FROM OLEFIN OXIDES AND AMMONIA

Two major series of compounds are included within this class of materials. The first series, the *ethanolamines*, includes mono-, di-, and triethanolamine ($\text{NH}_2\text{C}_2\text{H}_4\text{OH}$, $\text{NH}(\text{C}_2\text{H}_4\text{OH})_2$, and $\text{N}(\text{C}_2\text{H}_4\text{OH})_3$, respectively). Ethanolamines were first prepared in 1860 by Wurtz, who heated ethylene chlorohydrin with aqueous ammonia in a closed tube. Ethanolamines were first separated in 1897 by Knorr, who used fractional distillation methods (22). It was not until 1928, however, that triethanolamine was produced commercially, and not until 1931 that mono- and diethanolamines became available on a large scale. In recent years, a number of variously substituted ethanolamines, namely, aminoethylethanolamine, diethylethanolamine, and dimethylethanolamine, have become important commercially.

The second major series of alkanolamines is comprised of the "*isopropanolamines*" (2-propanolamines), products in which at least one ammonia hydrogen is replaced by the 2-hydroxypropyl ($-\text{CH}_2\text{CHOHCH}_3$) radical. Commercially important isopropanolamines include mono-, di-, and triisopropanolamines ($\text{NH}_2\text{CH}_2\text{CHOHCH}_3$, $\text{NH}(\text{CH}_2\text{CHOHCH}_3)_2$, and $\text{N}(\text{CH}_2\text{CHOHCH}_3)_3$). The 3-hydroxypropyl ($-\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$) derivatives have also been prepared but are not well known, since starting materials are not readily available. Other propanolamines available in semi-commercial or research quantities include dimethylisopropanolamine, *o*-tolylpropanolamine, and dibutylisopropanolamine.

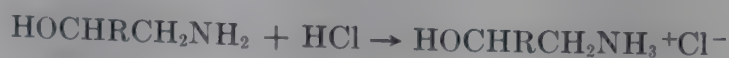
Properties

The ethanolamines and monoisopropanolamines are colorless liquids at room temperature or slightly above, whereas di- and triisopropanolamines are white solids. The density of the ethanolamines is slightly higher than that of water; the density of the isopropanolamines, slightly lower.

Alkanolamines are miscible in all proportions with water and alcohol. Ethanolamines are almost completely insoluble in nonpolar solvents, such as ether, but isopropanolamines are completely miscible with ether. Ethanolamines and isopropanolamines have a mild ammoniacal odor, show marked hygroscopic tendencies, and react readily with acid gases, such as carbon dioxide and hydrogen sulfide. Table 1 summarizes the properties of the more important and interesting alkanolamines (3,19).

The alkanolamines can react as amines, as alcohols, and in other ways. Their chemistry is thus decidedly complex. This section summarizes their most important reactions, organized according to types of compounds involved.

Acids. The reaction of alkanolamines with the halogen acids and organic acids of high dissociation constant, such as *p*-nitrobenzoic acid and trichloroacetic acid, leads to the formation of crystalline salts.



$\text{HOCHRCH}_2\text{NH}_2$ is written as a generalized expression covering ethanolamine ($\text{R} = \text{H}$) as well as isopropanolamine ($\text{R} = \text{CH}_3$).

Long-chain fatty acids, such as oleic and stearic, combine with alkanolamines at room temperature to give neutral alkanolamine soaps, such as $\text{HOCHRCH}_2\text{NH}_2 \cdot \text{HOOC}\text{C}_{17}\text{H}_{35}$. These products are waxy, noncrystalline materials which have widespread commercial application as emulsifiers.

Table 1. Properties of Alkanolamines

Common name	Chemical Abstracts name	Formula	Freezing point, °C	Boiling point, °C, 760 mm Hg ^a	Specific gravity, 20/20°C ^a	Viscosity, cps, 20°C ^a	Solubility, approx, g/100 g
monoethanolamine	2-aminoethanol	NH ₂ C ₂ H ₄ OH	10.3	171	1.0179	24.1	∞
diethanolamine	2,2'-iminodiethanol	NH(C ₂ H ₄ OH) ₂	27.5	187, 50 mm Hg	1.0919, 30/20°C	380, 30°C	∞
triethanolamine	2,2',2''-nitrilotriethanol	N(C ₂ H ₄ OH) ₃	17.9	360	1.1258	1013	∞
methyl ethanolamine	2-methylaminoethanol	NH(CH ₃)C ₂ H ₄ OH	-4.5	159.7	0.9414	13.2	∞
methyl diethanolamine	2,2'-(methylimino)diethanol	N(CH ₃)(C ₂ H ₄ OH) ₂	-21.0	247.2	1.0418	101	∞
dimethyl ethanolamine	2-dimethylaminoethanol	N(CH ₃) ₂ C ₂ H ₄ OH	-59.0	134.6	0.8879	3.8	∞
diethyl ethanolamine	2-diethylaminoethanol	N(C ₂ H ₅) ₂ C ₂ H ₄ OH		162.1	0.8851	3.5	∞
butyl ethanolamine	2-butylaminoethanol	NH(C ₄ H ₉)C ₂ H ₄ OH	-2.1	199.3	0.8932	20.2	∞
dibutyl ethanolamine	2-dibutylaminoethanol	N(C ₄ H ₉) ₂ C ₂ H ₄ OH	-75 ^e	228.7	0.8615	7.7	0.4
diisopropyl ethanolamine	2-diisopropylaminoethanol	N(C ₃ H ₇) ₂ C ₂ H ₄ OH	-39.3	190.9	0.8760	7.7	1.2
aminoethyl ethanolamine	2-(2-aminoethylamino)ethanol	NH ₂ C ₂ H ₄ NHC ₂ H ₄ OH		243.7	1.0304	141	∞
di(2-ethylhexyl)ethanol-amine	2-bis(2-ethylhexyl)amino-ethanol	N(C ₈ H ₁₇) ₂ C ₂ H ₄ OH	-60 ^e	216	0.8573	35.1	<0.1
ethyl diethanolamine	2,2'-(ethylimino)diethanol	N(C ₂ H ₅)(C ₂ H ₄ OH) ₂		167	1.0156	86.8	∞
N-acetyl ethanolamine	N-2-hydroxyethylacetamide	NH(COCH ₃)C ₂ H ₄ OH	15.8	decomp	1.1223	203	∞
phenyl ethanolamine	2-anilinoethanol	NH(C ₆ H ₅)C ₂ H ₄ OH	10.6 ^d	193	1.0970	101	4.6
phenyl diethanolamine	2,2'-(phenylimino)diethanol	N(C ₆ H ₅)(C ₂ H ₄ OH) ₂	56.6 ^d		1.1203, 60/20°C	119, 60°C	2.8
phenylethylethanolamine	2-N-ethylanilinoethanol	N(C ₆ H ₅)(C ₂ H ₅)C ₂ H ₄ OH	37.2	185	1.04		0.2
monoisopropanolamine	1-amino-2-propanol	NH ₂ CH ₂ CHOHCH ₃	-2	159.2	0.960, 25/25°C	30.2	∞
diisopropanolamine	1,1'-iminodi-2-propanol	NH(CH ₂ CHOHCH ₃) ₂	39	248.2	0.992, 40/4°C	198, 45°C	∞
triisopropanolamine	1,1',1''-nitrilotri-2-propanol	N(CH ₂ CHOHCH ₃) ₃	58	300.1	0.9909, 60/20°C	138, 60°C	∞
dibutylisopropanolamine	1-dibutylamino-2-propanol	N(C ₄ H ₉) ₂ CH ₂ CHOHCH ₃	-80 ^e	229.1	0.8419	3.5	<0.1
dimethylisopropanolamine	1-dimethylamino-2-propanol	N(CH ₃) ₂ CH ₂ CHOHCH ₃	-85 ^e	125.8	0.8512		
N-(2-hydroxypropyl)-ethylenediamine	1-(2-aminoethylamino)-2-propanol	NH(C ₃ H ₆ OH)C ₂ H ₄ NH ₂	180,	114 mm Hg	0.9859, 25/25°C	112, 25°C	∞

^a Unless otherwise specified. ^b In H₂O at 25°C. ^c Sets to a glasslike solid below this temperature. ^d Melting point.

When these alkanolamine soaps or mixtures of alkanolamines and fatty acids in proportions other than those resulting in soaps are heated (140–160°C), with or without a catalyst, a variety of reactions are possible (31). Products may be as follows:

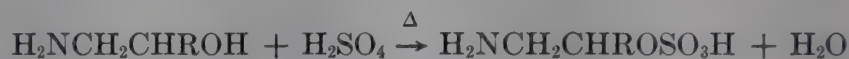
amides	$\text{HOCHRCH}_2\text{NHCOR}'$
amine esters	$\text{R}'\text{COOCHRCH}_2\text{NH}_2$
amide esters	$\text{R}'\text{COOCHRCH}_2\text{NHCOR}'$

When dialkanolamines are the starting materials, both mono- and diesters can be formed, so that the number of possible chemical species, among which interconversions are possible, is considerable. Some derivatives of piperazine, $\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2$, are also formed.

Two series of industrial products, both *alkanolamides*, are made by heating alkanolamines and fatty acids, either in a 1:1 ratio, or in a 2:1 ratio (see under Uses).

Trialkanolamines cannot form amides, since there is no hydrogen attached to the nitrogen. If trialkanolamines are heated with fatty acids at a temperature high enough to eliminate water, esters can be formed, up to the triesters, $\text{N}(\text{CH}_2\text{CHROO-CR}')_3$.

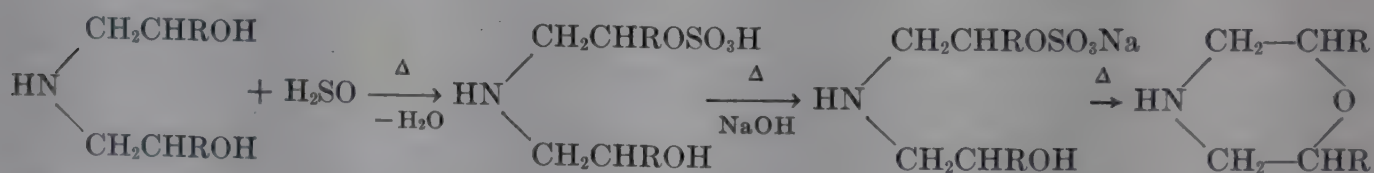
Heating of alkanolamines with sulfuric acid leads to the formation, by reaction of the hydroxyl group, of monoesters of sulfuric acid.



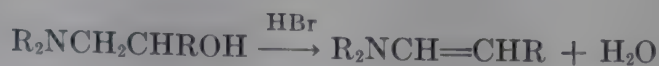
Subsequent heating in the presence of sodium hydroxide results in dehydration. Thus, monoalkanolamines can be dehydrated to form 2-alkylaziridines (4,34,53).



In a similar manner, diethanolamine and diisopropanolamine can be dehydrated to give morpholine and 2,6-dimethylmorpholine (26).



When nitric acid is substituted for sulfuric acid, the corresponding esters of nitric acid are formed. With concentrated (48%) hydrobromic acid, α,β -unsaturated amines result.



Esters, Aldehydes. The reaction of esters with alkanolamines at a temperature of 110°C involves the amine group of the latter and results in *N*-alkyl amides.

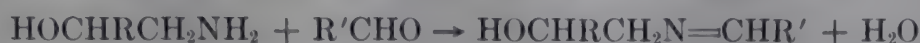


Subsequently, the hydroxyl group can be made to undergo reaction with an acyl halide, and to yield the ester amide.

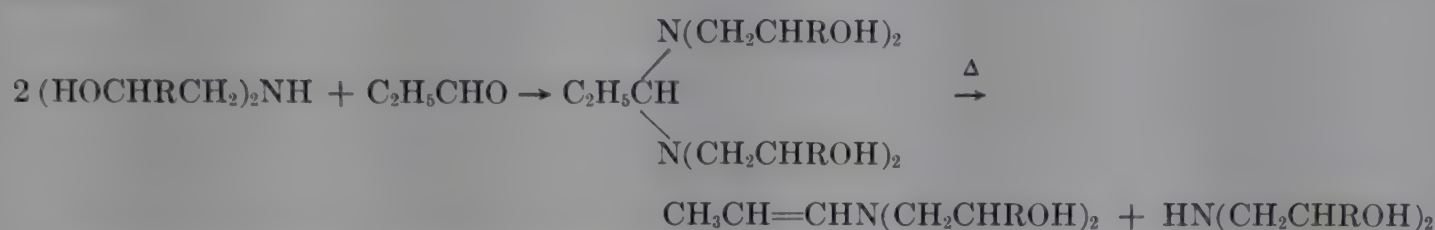


The reaction of the methyl esters of fatty acids with alkanolamines is utilized commercially to prepare high-purity 1:1 alkanolamides (see under Uses). These products, in contrast to the 1:1 alkanolamides prepared from the parent fatty acids, contain only a small quantity of by-products or unreacted starting materials.

The reaction of primary alkanolamines with aliphatic and aromatic aldehydes (other than formaldehyde) results in the formation of Schiff bases.



With secondary alkanolamines, aldehydes in the presence of K_2CO_3 yield di-*tert*-amines, which on distillation break down into α,β -unsaturated amines and secondary amines.



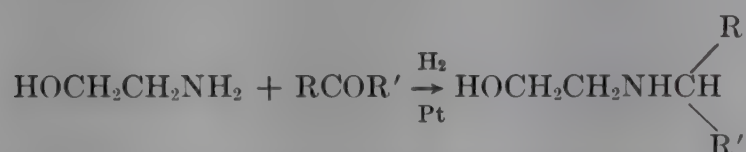
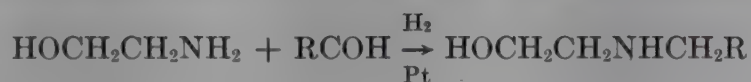
Formaldehyde combines with primary and secondary alkanolamines in the presence of alkali to give methylol derivatives.



These products may undergo further reaction with a second mole of amine, as follows:

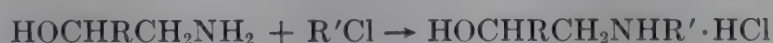


Mixtures of ethanolamine with aldehydes or ketones may be catalytically reduced with a platinum oxide-platinum catalyst to give 2-alkylaminoethanols (13).



The reaction is carried out under nitrogen in an inert solvent, such as benzene. Generally, no heating is required.

Alkyl and Aralkyl Halides. Alkyl halides form *N*-alkyl derivatives when reacted with alkanolamines.



With aralkyl halides in which the aryl group is either a benzene or a naphthalene residue, the following reaction takes place.



Thionyl Chloride, Phosphorus Pentachloride. With reagents such as thionyl chloride or phosphorus pentachloride the hydroxyl group may be replaced by a chlorine atom. For example, ethyldiethanolamine treated with thionyl chloride in chloroform solution on a water bath gives a 79% yield of 2,2'-dichlorotriethylamine (25).

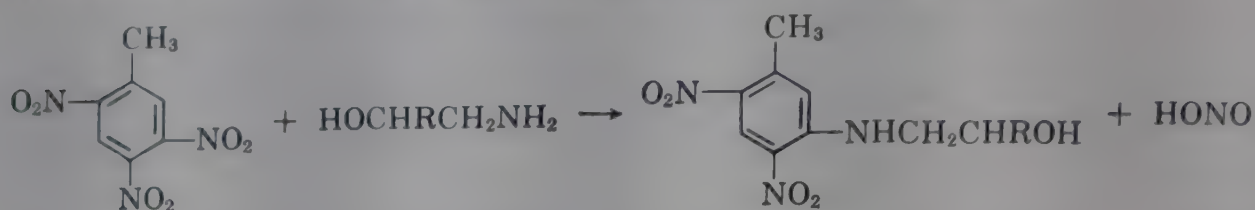


Polymer Formation. Under the proper conditions, polyester polyamides are formed by the addition of a dicarboxylic acid to a monoalkanolamine (32). The addi-

tion of ethylene oxide or propylene oxide to trialkanolamine is said to produce compounds having the formula $N((CH_2CHRO)_xH)_3$ (49).

Other Reactions. Additional types of compounds which can be used to prepare *N*-substituted alkanolamines include alkylidene halides, alkyl sulfates, arylsulfonyl halides, nitroaryl halides and dihalides, phthalic acid and phthalic anhydride (16).

With 2,4,5-trinitrotoluene, alkanolamines react as shown below.

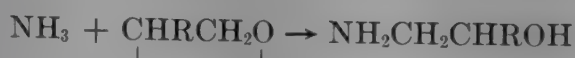


In certain cases, the alkanolamines function as reducing agents. Thus, monoethanolamine may be used to reduce anthraquinone to anthranols, acetone to 2-propanol, and azobenzene to aniline (38). This reaction depends on the decomposition of the alkanolamine into ammonia and an aldehyde. Similarly, diethanolamine converts *o*-chloronitrobenzene to 2,2'-dichloroazobenzene and *m*-dinitrobenzene to 3,3'-diaminoazobenzene (39).

Ethanolamine may be converted to piperazine by passing ammonia-ethanolamine mixtures over a metal hydrogenation catalyst at elevated temperatures and pressures (36). With a pressure of 2000 psi, a temperature near 200°C, and a 5:1 ammonia-ethanolamine ratio, piperazine is obtained in 25–30% yield, along with ethylenediamine and diethylenetriamine. By altering the reaction conditions, piperazine yields may be reduced, and the yield of the other products increased.

Manufacture

Alkanolamines are prepared commercially by the reaction of ethylene oxide or propylene oxide with ammonia (46,54).



The reaction is exothermic and is usually carried out at temperatures of 50–100°C under pressures of 150–300 psi. It may be run, at controlled temperature and pressure, either in a coil-type reactor by continuously pumping aqueous ammonia and alkylene oxide into the coil, or in a kettle-type reactor by slowly pumping the oxide into the ammonia solution in the agitated kettle. Because water aids temperature control by removing heat of reaction, most commercial processes use 28–50% aqueous ammonia. However, Lowe (35) has developed a technique requiring only low concentrations of water or an organic hydroxy compound, and Schwoegler (47) has claimed an anhydrous process. Other modifications of this process are those of Olin and Schwoegler (43) and of Reid and Lewis (44,45). Figure 1 is a flowsheet for a typical ethanolamine manufacturing plant.

The relative proportions of mono-, di-, and trialkanolamines that can be obtained by the above procedure is dependent upon the ratio of ammonia to alkylene oxide used. A large excess of ammonia favors the formation of the monoalkanolamine. Control of the final products may also be achieved by a recycle technique, wherein an

excess of the unwanted mono- or dialkanolamine is added to the ammonia-alkylene oxide reaction mixture (21). The addition of excess monoethanolamine (MEA) makes it possible to suppress the formation of this material and to obtain, as a reaction product, a mixture consisting almost entirely of di- and triethanolamine (DEA and TEA). The addition of a mixture of di- and triethanolamine, however, will not promote the formation of monoethanolamine.

Alkylene oxides will react with nearly all nitrogen compounds having one or more hydrogens attached to the nitrogen. Thus, a large number of mixed alkanolamines can be made by reacting ethylene oxide, under the conditions described for the reaction with ammonia, with such alkanolamines as mono- and diisopropanolamine, or by reacting propylene oxide with mono- or diethanolamine (28). Other types of amines besides alkanolamines may also be used as starting materials. Thus, aminoethyl-ethanolamine is prepared by reacting ethylenediamine with ethylene oxide, and *N*-(2-hydroxypropyl)ethylenediamine by reacting ethylenediamine with propylene oxide.

Although the reaction of alkylene oxides and ammonia is the chief commercial method for the preparation of alkanolamines, other means of synthesizing these products have also been developed. For example, preparation may be carried out by the ammonolysis of a halohydrin (8,33).



With this method, difficulties are encountered in separating the amines from the ammonium chloride also formed by the reaction.

The hydrogenation of formaldehyde cyanohydrin in the presence of a nickel catalyst yields mono- and diethanolamine (24).



Hydrogenation of nitro alcohols under elevated temperatures and pressures and in the presence of nickel catalyst and small amounts of carbon dioxide gives alkanolamines (20). Electrolytic reduction or reduction by means of iron and an acid are also satisfactory.

Monopropanolamines have been made by the hydrogenation of ethylene cyanohydrin (27) and by the hydration of acrolein, treatment with ammonia, and subsequent hydrogenation of the reaction product (6).

Economic Aspects

Because of the lack of published statistics on the isopropanolamines, figures on the total yearly production of alkanolamines in the United States are virtually impossible to obtain. However, production figures for the ethanolamines, which account for an estimated 90–95% of the total, are available and are presented in Table 2 (11,29).

The increase in the production of ethanolamines during the years 1947–1956 resulted directly from the growth of the synthetic-detergent (syndet) industry. In particular, this increase reflects the growing acceptance of liquid household syndets, many of which are based on ethanolamine. A second important factor in the growth of ethanolamines production is their expanding use in gas purification.

The prices of the corresponding ethanolamines and isopropanolamines are comparable. In May, 1962, both monoethanolamine and monoisopropanolamine were selling for 25¢/lb in tank-truck quantities. Prices for diethanolamine and diisopropanolamine in similar quantities were 24.5¢/lb and 20.75¢/lb, respectively.

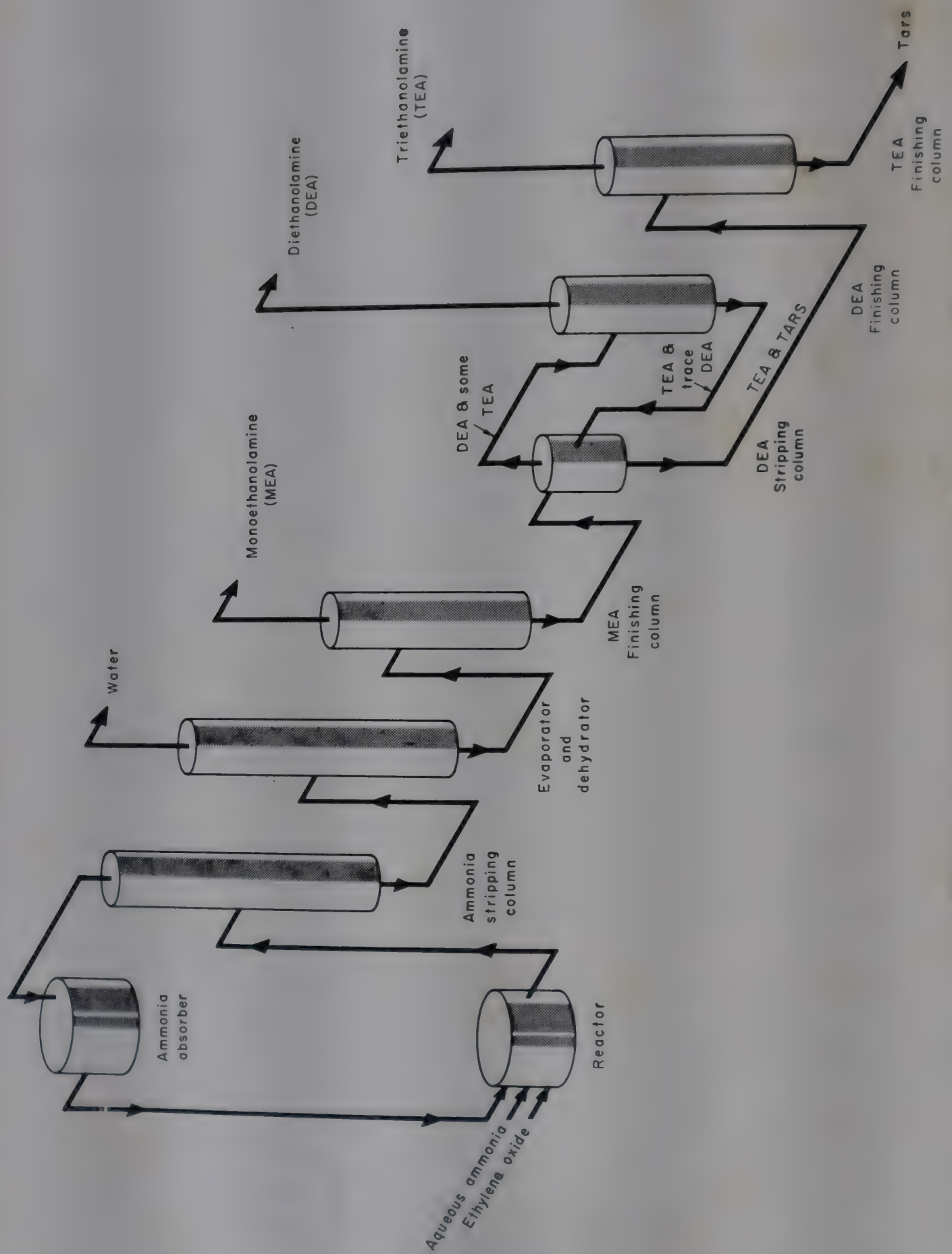


Fig. 1. Flowsheet for the production of ethanolamines.

Table 2. Annual United States Production of Ethanolamines

Year	Production, thousands of pounds			
	Total ^a	MEA	DEA	TEA
1937	4,000 ^a			
1939	5,700 ^a			
1943	23,000 ^a			
1947	40,000 ^a			
1954	62,885	23,511	22,755	16,619
1956	93,359	29,147	40,428	23,784
1958	97,384	30,614	40,654	26,116
1960	123,000 ^b			

^a Further breakdown unavailable.
^b Preliminary figure.

Specifications

Table 3 gives specifications for some of the more important alkanolamines (3,18). The alkanolamines are shipped in aluminum or stainless-steel tank cars and tank trucks, and in steel drums. No special precautions are required for shipment of the alkanolamines.

Table 3. Specifications of Some Alkanolamines

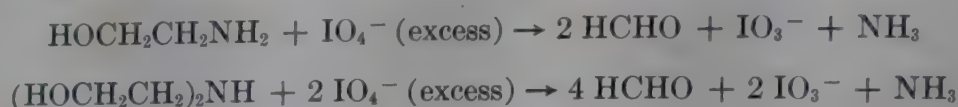
Compound	Assay, minimum, %	Equivalent weight, apparent	Boiling range, ibp-dec pt, °C, 760 mm Hg	APHA color, maximum	Specific gravity		Water maximum, %
					25/25°C ^d	20/20°C ^d	
monoethanolamine	99.0	61-62	166-174	15	1.017-1.021	1.014-1.018	1.0
diethanolamine	98.5	104-106		20	1.091-1.096 (30/25°C)	1.090-1.095 (30/20°C)	0.15
triethanolamine	85.0	140-145		75	1.122-1.130	1.120-1.128	0.2
aminoethylethanolamine	99.0		242-246	100	1.028-1.033	1.026-1.031	
diethylethanolamine		116-117.8	157-165	15		0.880-0.890	0.2
methyldiethanolamine		118-120	242-260	200		1.040-1.044	0.5
monoisopropanolamine	98.5	75-76	156-165	20	0.958-0.962	0.960-0.964	0.5
diisopropanolamine		132-134		40			0.5
triisopropanolamine		189-192		100 ^a			0.5
di- and triisopropanolamine, mixed ^b		155-165			1.020-1.030		14-16
isopropanolamines, ^c mixed		137-143		100		0.002-0.012	0.5

^a 50% aqueous solution.
^b Diisopropanolamine, 72% minimum; triisopropanolamine, 12% maximum.
^c Monoisopropanolamine, 10-15%; di- and triisopropanolamine, 40-50% each.
^d Unless otherwise specified.

Analytical and Test Methods

Determination of the assay of alkanolamines varies according to the amine type. With monoethanolamine and monoisopropanolamine, the procedure is relatively simple; an accurately weighed sample of the amine is titrated with standard hydrochloric acid in the presence of methyl red indicator and the percentage of amine is calculated in the usual manner.

The assay determination for diethanolamine or diisopropanolamine involves several steps. The sample is first treated with an excess of periodate, which reacts with both mono- and dialkanolamine according to the equations,



The excess periodate is reduced with an excess of arsenite, which is finally titrated with standard iodine solution.

The monoalkanolamine is then determined by a modified Van Slyke procedure, and the above titration is corrected accordingly.



As an alternative to the Van Slyke method, a colorimetric procedure may be employed. The monoalkanolamine is reacted with copper salicylaldehyde, the product extracted with 1-hexanol, and the color developed by *N,N'*-di(hydroxyethyl)dithiocarbamic acid reagent.

Trialkanolamine is determined by initial treatment with acetic anhydride, which forms amides with the primary and secondary alkanolamines, as shown below.



The trialkanolamines, which are without *N*-hydrogen, do not react. The unreacted tertiary amine is then titrated with an alcoholic solution of hydrochloric acid. The acetic acid liberated in the first reaction has essentially no effect on the potential of the system, but the appearance of an excess of hydrochloric acid gives a sharp change in potential which is detected either potentiometrically or by the use of a mixed indicator containing methyl orange and xylene cyanol FF. The monoalkanolamine and dialkanolamine are then determined by the periodate and the Van Slyke procedures.

The apparent equivalent weight of alkanolamines is computed from the total alkalinity, which is determined by titration with standard hydrochloric acid. Boiling range and specific gravity are determined by ASTM procedures, with or without minor modifications. The first is determined essentially by ASTM Method Designation D1078; the second by Method C of ASTM Designation D891. Water content is determined by titration with Karl Fischer reagent, color by comparison of a sample of the alkanolamine with APHA color standards. Detailed analytical procedures for the various alkanolamines are usually available from producers.

Materials for Storage and Handling

Ordinary steel or black-iron containers are satisfactory for storing alkanolamines unless discoloration cannot be tolerated, in which case stainless steel or aluminum is recommended. Copper, brass, or other copper alloys are readily attacked by the alkanolamines and should never be used with them. Storage tanks for undiluted

alkanolamines are ordinarily equipped with steam-heating coils and are padded with a dry inert gas such as nitrogen to prevent discoloration.

Transfer lines should be of stainless steel, and may be steam-traced for use in cold weather. No rubber hose should be used since ethanolamines attack rubber. Steel, black iron, or stainless pumps are suitable for alkanolamine service. Blue asbestos is satisfactory for pump packing. Commonly accepted gasket materials include superheat asbestos for process lines and equipment, and polyethylene fittings for drums. Joints should preferably be flanged or welded since conventional pipe dopes are leached out by alkanolamines.

Health and Safety Factors

The ethanolamines and isopropanolamines have low oral toxicity. The LD_{50} for rats is 2.13 g/kg of body weight for diethanolamine and 9.85 g/kg of body weight for triethanolamine, with LD_{50} 's for other common alkanolamines falling between these values. Thus, there is no appreciable hazard from ingestion incidental to normal industrial handling. Serious toxic effects may, however, result if substantial quantities are swallowed. Vapors of these products present no inhalation hazard at ordinary temperatures. Excessive concentrations of vapor may occur on heating, but these are sufficiently irritating to the eyes and nose to give ample warning of their presence.

All of the ethanolamines and isopropanolamines have a significant irritating action on the eyes, and most, likewise, have an appreciable local irritating action on the skin. This action appears to be somewhat more pronounced with monoethanolamine and monoisopropanolamine than with higher members of the series. In general, serious eye injury will result only in the absence of proper medical care, and serious skin injury only upon repeated or prolonged contact.

To avoid eye contamination, persons handling alkanolamines should wear full face shields and goggles with side shields or the equivalent. If eyes are contaminated, they should be washed with flowing water for at least 15 minutes and a physician should be called immediately. In the event of skin contact with the ethanolamines, contaminated shoes and clothing should be removed and the skin thoroughly washed with water. If an alkanolamine is swallowed accidentally, vomiting should be induced as quickly as possible and medical attention obtained without delay.

A portion of the above information is made available by the courtesy of Busby Run Laboratory of Mellon Institute, Chemical Hygiene Fellowship, supported by Union Carbide Chemicals Company.

Uses

The alkanolamines find unusually diverse industrial application, as indicated by Table 4, which lists major uses for the ethanolamines (1). (See Detergency; Emulsions; Surfactants.)

Ethanolamines and isopropanolamines are utilized most often in the form of either alkanolamides or alkanolamine soaps. Alkanolamides, which form an important class of the fatty amides (see also Amides), are nonionic detergent materials. They are manufactured by condensing an alkanolamine with a fatty acid or acid ester at elevated temperatures. When monoethanolamine or monoisopropanolamine are the starting amines, *monoalkanolamides*, $HOCHRCH_2NHCOR'$, are the products; with diethanolamine and diisopropanolamine as the starting amines, *dialkanolamides*,

Table 4. Major End Uses for Ethanolamines

Use	Consumption, millions of pounds		
	1950	1955	1960
detergents	8	25	43
gas and oil purification	4	21	29
cosmetics	5	8	13
textile specialties	4	11	20
agricultural products	6	2	2.5
emulsion polishes	4	6	8
other uses	3	5	10

(HOCHRCH₂)₂NCOR', are the products. The two types of alkanolamides available are those prepared by reacting the starting materials in a 1:1 ratio, and those prepared by reactions in which a 2:1 ratio of alkanolamine to acid or ester is used.

Optimum detergency and foam stability are obtained with lauric acid, therefore this material is the chief fatty acid used in preparing both 1:1 and 2:1 amides. Other acids which may be employed include oleic, stearic, myristic, and coconut fatty acids.

The 1:1 alkanolamides can be prepared with or without the use of a sodium meth-ylate catalyst. The catalyst decreases side reactions and gives a product which may contain over 95% amide as compared to 88–95% amide obtained without catalysts. These catalyzed amides exhibit improved detergency and foam stability. They are frequently sold under the designation "super amides" or "extra amides." Aqueous solubilities range from limited for the noncatalyzed 1:1 amide to almost completely insoluble for the catalyzed.

The 2:1 alkanolamides contain about 60% amide and 40% side products or unreacted starting materials and have greater aqueous solubility than the 1:1 products.

Collectively, alkanolamides range from amber liquids to white, waxy solids. They may be odorless or have a slightly ammoniacal odor. They usually have a pH between 9 and 10.

Alkanolamides are used chiefly as detergents and detergent additives. They are believed to be constituents of many of the current commercial household detergents (1). Miscellaneous applications include use as drycleaning soaps, fuel-oil additives, rust inhibitors, latex stabilizers, textile-scouring and antistatic compounds, dye-leveling agents, waterproofing-formulation ingredients, and wax and resin additives (1).

Monoalkanolamides are used primarily in heavy-duty powder detergents as foam stabilizers, corrosion inhibitors, and rinse improvers. Desirable characteristics in this application include excellent resistance to high alkalinity, superior foam-boosting properties, and increased grease-solubilizing capacity. The monoalkanolamides also serve as water-in-oil emulsifiers for pharmaceuticals and agricultural preparations and in textile processing.

The dialkanolamines are used in the cosmetics industry as shampoo thickeners, foam improvers, hair conditioners, rinse improvers, and opacifying agents. In general, dialkanolamides are useful in detergent products, such as light-duty powder detergents and heavy- and light-duty liquid detergents, where high alkalinity is not encountered and high solubility is imperative.

Alkanolamine soaps rank close behind the alkanolamides as important industrial products. They are formed by reaction of an ethanolamine or isopropanolamine with a fatty acid, a reaction similar to the formation of alkanolamides, but one that is car-

ried out at a lower temperature and without a catalyst. As a result, a loosely bonded addition product (salt), rather than an amide, is obtained. These products are approximately neutral in pH and display solubility in both water and hydrocarbon solvents. Very stable oil-in-water emulsions can be prepared with alkanolamine soaps. Such emulsions are characterized by small particle size, high stability, and noncorrosiveness. They are easy to prepare and usually require 10–20% of the soap, based on the weight of the material to be emulsified, for complete emulsification.

The alkanolamines most commonly used to prepare alkanolamine soaps are monoethanolamine, monoisopropanolamine, and triethanolamine. These products are employed because they produce emulsions having finer particle size and greater stability than other alkanolamines. The chief fatty acids utilized in the preparation of alkanolamine soaps are oleic, stearic, and palmitic. Oleic acid is selected for emulsions of low viscosity, and stearic acid for emulsions of high viscosity or when a pure white or pearlescent emulsion is desirable. Alkanolamine soaps vary in consistency from clear materials resembling petroleum jelly to hard, white products.

Soaps made from triethanolamine and the isopropanolamines are extensively employed in cosmetic preparations, such as cold cream, cleansing cream, vanishing cream, suntan lotion, shaving cream, and shampoos. The low alkalinity of these soaps is especially important, since cosmetics must be nonirritating to the skin and non-injurious to fabrics.

In the preparation of weed-killer formulations, alkanolamines are reacted with (2,4-dichlorophenoxy)acetic acid (2,4-D) to form the corresponding salts. Formulations prepared in this way are emulsions which display excellent resistance to solidification when stored at low temperatures and which are less volatile than formulations containing 2,4-D esters. The emulsion breaks immediately when sprayed onto a surface, thus its herbicidal action is considerably speeded up (2).

The textile industry utilizes alkanolamine soaps as knitting oils for wool and rayon. These soaps yield a soft, easily dyed fabric, reduce clogging of the needles by gum, and decrease sinker corrosion. Unreacted alkanolamines, in particular, triethanolamine, are also utilized as gas-fading inhibitors, and scouring and fulling aids for wool and worsteds (2,3). Aqueous solutions of monoethanolamine sulfite are employed for imparting permanent creases to wool.

Large quantities of alkanolamine soaps are consumed in the manufacture of a wide range of household and industrial specialties. Specific types of products include "soluble" lubricating and cutting oils; floor, furniture, automobile, and metal polishes; solvent cleaners, stain and paint removers, and spotting soaps; and floor, rug, woodwork, and paintbrush cleaners (2).

The most important application for the straight ethanolamines is the sweetening of natural gas (23). The procedure involves the reaction of the aqueous ethanolamine with the H_2S , CO_2 , and other acidic constituents of the gas to give a water-soluble salt, followed by steam stripping of the amine. In general, monoethanolamine is used for natural gas treatment because of its lower equivalent weight. Diethanolamine must be used, however, if there is a significant quantity of carbonyl sulfide in the gas since this material forms an unregenerable complex with monoethanolamine. Advantages of diethanolamine over monoethanolamine in treating refinery gases include lower vapor pressure and hydrocarbon solubility.

In a typical gas-sweetening unit, the sour gas first passes into the base of an absorber and flows upward, countercurrent to a dilute (10–20%) amine–water solution

which removes the acid constituents. The contact temperature is usually 80–120°F, and pressures ranging from atmospheric to well over 1000 psig have been employed successfully. The sour amine solution is heated to 220–240°F and passed through a regenerator, which strips out all but trace quantities of the H_2S and CO_2 . The regenerated amine solution is recycled, while the acid gases are burned, released to the atmosphere, or processed as by-products. When oxygen or cyanide is present along with H_2S in the gas stream, amine thiosulfate or amine thiocyanates are formed in the amine-treating solution. These are not regenerated in the still column and eventually build up to the point where the acid-gas capacity of the amine is seriously reduced. When this occurs, the amine may be recovered by adding soda ash to the treating solution. The soda ash reacts with the amine thiosulfate or thiocyanate to form the corresponding sodium salt and amine carbonate. The amine carbonate is decomposed in the still and the amine solution is regenerated in the usual manner. With monoethanolamine the sodium salts are removed in an atmospheric side-stream reclaimer still. With diethanolamine, a vacuum still or molten salt bath must be used. The amine-sweetening process is efficient, economical, and relatively trouble-free, although attention must be paid to prevention of corrosion.

Although the sweetening of natural gas is the most important application for the alkanolamines, other significant uses also exist. Alkanolamines are excellent corrosion inhibitors. One of the early uses for triethanolamine was in acid pickling baths (15). Triethanolamine salts, such as triethanolamine phosphate, prevent corrosion by ethylene glycol-based antifreeze solutions (12,14). During World War II, approximately 10% of the entire production of triethanolamine was employed in aircraft engine coolants (51). Alkanolamines are also incorporated into brake fluids to inhibit corrosion. Mixtures of alkanolamines, for example, a 50-50 mixture of triethanolamine and diethanolamine, are used in formulating carbon-removal compounds for aircraft engine pistons (52).

The alkanolamines are employed for copper-electroplating operations (9), in photographic developers (50), and as soldering fluxes (40). A mixture of triethanolamine and calcium salts of lignin sulfonic acid is used as an additive in portland cements (30). The mixture is added to the cement clinker during the grinding operations and permits finer grind without recourse to double burning or other expensive manufacturing operations. Concretes made from such additive-containing cement display increased early strength, improved freeze-thaw durability and workability, decreased bleeding, and lowered water permeability. When monoethanolamine is treated with carbon disulfide in alkali, the result is 2-mercaptothiazole, an accelerator in the vulcanization of rubber (42).

The pharmaceutical industry utilizes ethanolamine and isopropanolamine derivatives as analgesics, antihistamines, antispasmodics, local anesthetics, and burn remedies. The perchlorate salts of alkanolamines are reportedly (10) useful as oxidant additives in liquid fuels used for propelling rockets. The salts formed by condensation of boron trifluoride with alkanolamines are said (48) to have utility as wetting agents, bactericides, fungicides, herbicides, insecticides, rodent repellents, leveling agents for paints, and catalysts. The reaction of halogenated alkyl or alkoxyalkyl alkylene amines with dialkanolamines yields derivatives with surfactant and detergent properties (7).

Newer members of the alkanolamine family likewise find interesting uses. Aminoethylethanolamine derivatives find application as agricultural fungicides and insecti-

cides; as detergents, wetting agents, emulsifying agents, dyeing assistants, and modifying agents in textile processing; as chelating agents; and as gasoline stabilizers, emulsion breakers, extreme-pressure additives, and sulfurized-oil components in the petroleum industry (5).

Actual or potential applications for other alkanolamines and their derivatives are as follows (3):

Phenylethanolamine. Antirust compounds, lubricants, cutting oils.

Diethylethanolamine. Antirust compounds, emulsifiers for polish (55).

Phenyldiethanolamine, phenylethylethanolamine. Acetate rayon dyes.

N-Acetyethanolamine. Plasticizer for polyvinyl alcohol, cellulose, proteinoid substances; humectant for cellophane, textiles, paper, printing inks.

Dimethylethanolamine. Textile chemicals, polish ingredients, corrosion inhibitors, pharmaceutical intermediates.

Methyldiethanolamine. Textile, agricultural, and pharmaceutical chemicals; emulsifying agents; catalyst for urethane coating systems.

Propanolamines. Weed killers, light stabilizers for polystyrene (17,37).

N-(2-Hydroxypropyl)ethylenediamine. Curing agent for epoxy resins, intermediate for surface-active agents, resins, dyestuffs, pharmaceuticals, textile products, rubber products, insecticides, flotation agents (41).

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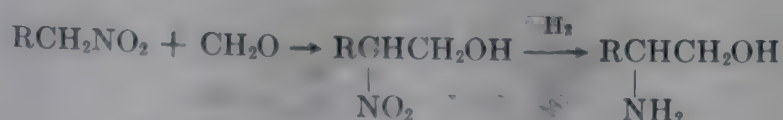
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ALKANOLAMINES FROM NITRO ALCOHOLS

The alkanolamines (amino alcohols) discussed here are obtained by reduction of nitro alcohols (qv) which are themselves obtained by condensation of nitroparaffins (qv) with aldehydes.



One, two, or three hydrogens on the carbon attached to the —NO_2 can be reacted with aldehydes, giving rise, after reduction, to amino alcohols with one, two, or three hydroxyl groups. The amino alcohols discussed here are listed in Table 1 with some of their properties. A comprehensive review of these compounds has been done by Hass and Riley (4).

Many other members of this series have been prepared but have not been marketed except in experimental or semicommercial quantities. The most notable of these are compounds with a carbon chain of up to six carbon atoms containing phenyl, methyl, and monohydroxy substitutions. *N*-substituted derivatives have also been prepared, and the *N,N*-dimethyl derivative of aminomethylpropanol is available in pilot-plant quantities.

Properties

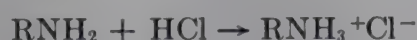
Physical Properties. Some physical properties of purified aminohydroxy compounds are given in Table 1. Except for 2-amino-1-butanol, these compounds are all crystalline solids at room temperature. Since 2-amino-2-methyl-1-propanol melts at slightly above room temperature, it usually appears as a paste rather than as a crystalline solid. The densities of these two compounds, when molten, are slightly less than that of water, but the densities of the other compounds are slightly higher than water. The densities of the crystalline materials vary considerably with crystal size.

The aminohydroxy compounds are nonflammable materials with high flash points. Aminomethylpropanol, for example, has a flash point of 155°F , Tag open cup. Also, their vapor pressures at ordinary temperatures are quite low so these properties cause no problems with respect to storage and handling.

All of these compounds are highly soluble in water; three of them are miscible. They are also very soluble in alcohols, slightly soluble in aromatic hydrocarbons, and nearly insoluble in aliphatic hydrocarbons. They have high boiling points and the polyhydroxy compounds are practically nonvolatile. They are weakly alkaline, but react with common organic and inorganic acids and acidic gases. The liquids have a mild, faintly amine odor, and the solids are nearly odorless.

Chemical Properties. These amino alcohols attack copper, brass, and aluminum, but are inert to steel and iron. Their toxicity is of a low order, and they present no unusual health hazards.

These compounds react to form salts with mineral acids.



The salts hydrolyze readily in the presence of water and dissociate due to heat. If a fatty acid, such as oleic, is employed, a soap is obtained. Such soaps, particularly those from AMP and AMPD, are highly efficient emulsifying agents and have many important industrial uses.

If the soap is heated further, the amide is formed, and on subsequent heating, the oxazoline ring is formed (3,12,24). However, if a dibasic acid is used with a diol, or triol, resins are formed (23). The reaction which yields an oxazoline is as follows.

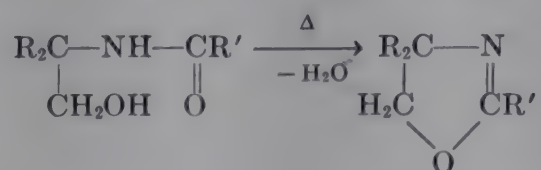


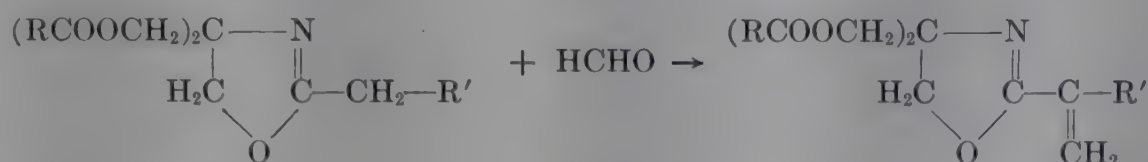
Table 1. Physical Properties of Purified Aminohydroxy Compounds

Compound	Formula	Mol wt	Boiling point, °C	Melting point, °C	Sp gr ^b	pH of 0.1M aq sol ^c	Solubility ^b in water, g/100 ml
2-amino-1-butanol (AB ^a)	$\begin{array}{c} \text{NH}_2 \\ \\ \text{CH}_3\text{CH}_2\text{CHCH}_2\text{OH} \end{array}$	89.14	178 ^d	-2	0.944	11.1	completely miscible
2-amino-2-methyl-1-propanol (AMP ^a)	$\begin{array}{c} \text{NH}_2 \\ \\ \text{CH}_3\text{CCH}_2\text{OH} \\ \\ \text{CH}_3 \end{array}$	89.14	165 ^d	30-31	0.934	11.3	completely miscible
2-amino-2-methyl-1,3-propanediol (AMPD ^a)	$\begin{array}{c} \text{NH}_2 \\ \\ \text{CH}_2\text{OHCCH}_2\text{OH} \\ \\ \text{CH}_3 \end{array}$	105.14	151-152 ^e	109-111		10.8	250
2-amino-2-ethyl-1,3-propanediol (AEPD ^a)	$\begin{array}{c} \text{NH}_2 \\ \\ \text{CH}_2\text{OHCCH}_2\text{OH} \\ \\ \text{C}_2\text{H}_5 \end{array}$	119.16	152-153 ^e	37.5-38.5	1.099	10.8	completely miscible
tris(hydroxymethyl)-aminomethane, 2-amino-2-(hydroxymethyl)-1,3-propanediol (THAM, Tris Amino ^a)	$\begin{array}{c} \text{NH}_2 \\ \\ \text{CH}_2\text{OHCCH}_2\text{OH} \\ \\ \text{CH}_2\text{OH} \end{array}$	121.14	219-220 ^e	171-172		10.4	80

^a Registered trademark of Commercial Solvents Corp.^b At 20°C.^c At 20/20°C.^d At 760 mm Hg.^e At 10 mm Hg.

These oxazoline derivatives have cationic surface-active properties and are water-in-oil emulsifying agents. They are acid acceptors and some exhibit corrosion-inhibiting properties. In the oxazolines from AMPD and AEPD one of the R's is $-\text{CH}_2\text{OH}$, and in the oxazoline from Tris Amino there are two $-\text{CH}_2\text{OH}$'s. These hydroxy groups can be easily esterified. With fatty acids they yield diesters. The oxazoline diesters from the saturated acids are synthetic waxes and those formed from unsaturated fatty acids are drying oils (8,13,18).

Formaldehyde will react with the α -carbon in these esters (that is, the α -carbon in the fatty acid from which the oxazoline was formed) to yield a vinyl group which can be heat-bodied to form linear polymers or utilized for further synthesis (9) (see under Uses). Thus, for the esters of the oxazoline formed from Tris Amino the following reaction occurs:



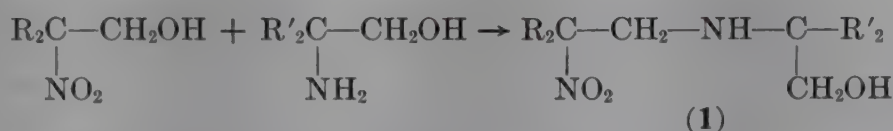
Products of this class are useful for modification of alkyd resins, for preparation of synthetic paint vehicles, and for production of copolymers with a variety of other monomers.

Substitution on the amino group occurs readily.

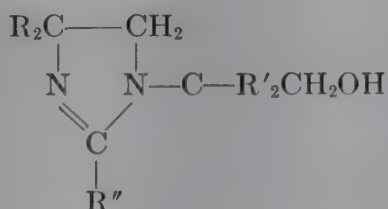


These compounds are stronger bases than the parent amines.

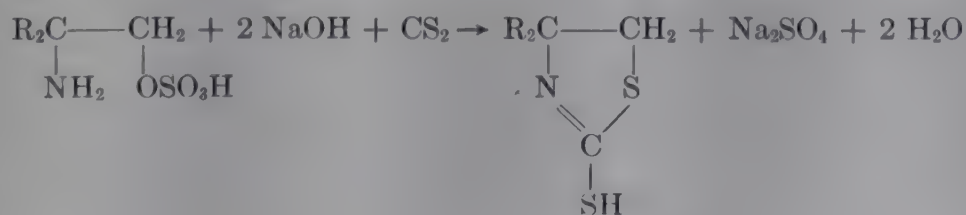
The aminohydroxy compounds react with nitro alcohols to form nitrohydroxyamines (1,5,7,22).



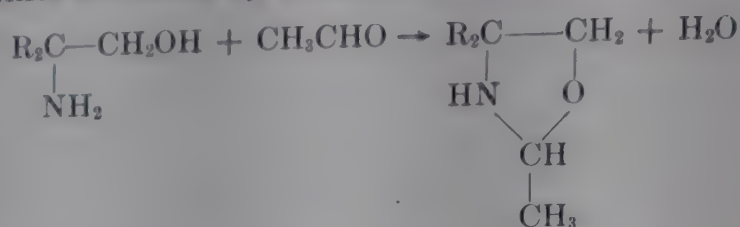
These compounds show bactericidal activity. They can be readily reduced ($-\text{NO}_2 \rightarrow -\text{NH}_2$) to form the hydroxydiamines. These diamines react with organic acids to form the amide which on further heating yields the imidazoline (17). Therefore, the diamine obtained by reducing (1), when reacted with an organic acid ($\text{R}''\text{COOH}$), gives the following:



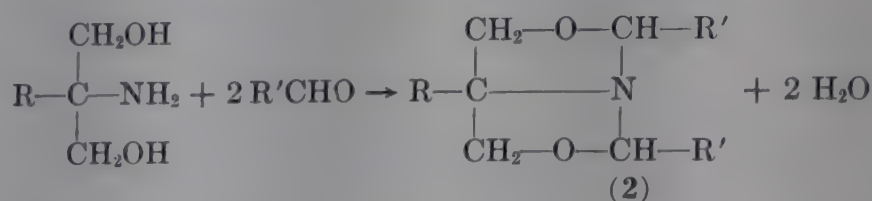
Substituted mercapto thiazolines are synthesized by sulfating the alcohol group with sulfuric acid, followed by reaction with carbon disulfide (15).



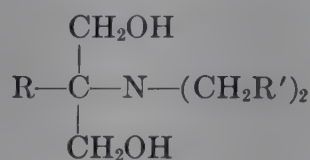
Substituted oxazolidines are made by condensation with aldehydes (6,11).



If an amino polyhydric alcohol is used with one mole of aldehyde, an oxazolidine also results, but if two moles of aldehyde are used, the result is a substituted 1-aza-3,7-dioxabicyclo [3.3.0] octane (2) (20).



These can be hydrogenated to *N,N*-substituted amino alcohols. Thus (2) yields



Oxidation of the hydroxy group leads to the formation of *amino acids*. For example, oxidation of aminomethylpropanol yields 2-methylalanine, $(\text{CH}_3)_2\text{CNH}_2\text{-COOH}$. The amino group is first protected by benzoylation, and the hydroxyl group is then oxidized with alkaline permanganate (2).

Manufacture, Economic Aspects, Specifications

The aminohydroxy compounds are prepared from the corresponding nitro alcohols by reduction. The reaction proceeds smoothly, even at room temperature, with common reducing agents (4,21). The aminohydroxy compound can react with the nitro alcohol to give nitro amines, or to decompose the nitro alcohol (in the presence of bases, nitro alcohols revert to the original nitroparaffin and formaldehyde), but these side reactions can be minimized by use of carbon dioxide to neutralize the amine group (4). The alkalinity is thus reduced and reactions at the amine group are minimized.

Table 2. Prices, per pound, of Aminohydroxy Compounds

	Tank car	Carload	Net weight, lb ^c
AB		\$1.25 ^a	425 D
AMP	\$0.42	0.44	420 D
AMPD crystals		0.95	200 F
AMPD concentrate		0.45	400 F
AEPD concentrate		0.55	440 D
Tris Amino		0.70	180 F
Tris Amino, 40% aqueous		0.45 ^b	500 D
2-dimethylamino-2-methyl-1-propanol		1.25 ^a	410 D

^a In semicommercial quantities, 1 drum or more.

^b 100% basis.

^c D = 55-gal steel drum.

F = Fiberpak.

2-Amino-1-butanol and AMP are purified by distillation, but AMPD and Tris Amino are purified by recrystallization. AEPD is available as the concentrate of the total reaction mixture and AMPD is also available in this form at a somewhat lower price than the purified compound.

There are no published production statistics on the aminohydroxy compounds, but they are selling in multimillion pound quantities with every indication of greatly increased volume in the next few years. Their use is increasing steadily as new applications are being discovered.

Prices for these products cover a rather broad range, but there has been good price stability for individual products. Table 2 gives 1961 figures for bulk quantities along with net weights when packaged in drum or Fiberpak.

The specifications found in Table 3 are applied to the semicommercial and commercially available compounds.

Table 3. Specifications for Aminohydroxy Compounds

Product	Neutral equivalent	Color, max	Water % wt, max	Distillation range, °C	Melting point, °C	Odor	Non-volatile matter, %
AB	92.0, max	40, APHA	1.0	170-185			
AMP	88.5-91.0	20, APHA	0.8	156-177		characteristic	0.005
AMP, low-melting ^a	90.0-92.5	20, APHA	2.0-2.8	135-177	20	characteristic	0.005
AMPD	103-107	^b	0.5		100, min		
AMPD concentrate	102-110 ^c	1, Gardner ^d	2				
AEPD concentrate	121.5, max ^e	2, Gardner	3.8				
Tris Amino	121-122	40, APHA ^e	0.5		160, min		

^a 2% water added to lower melting point from approximately 30°C to maximum of 20°C. Material containing 5% water is available on special order.
^b White to slightly off-white, free from foreign materials and lumps.
^c Anhydrous basis.
^d 25% aqueous solutions, Gardner (1933) scale. Color of molten product, Gardner 4, max.
^e 20% aqueous solution.

Uses

Until recently, these aminohydroxy compounds have been used principally as emulsifying agents in the form of soaps of oleic acid. Recent advances in resin technology, however, have led to applications in that field. Tris Amino also has several applications not shared by any of the other alkanolamines.

2-Amino-2-methyl-1-propanol. This product forms soaps with fatty acids, which are very powerful emulsifying agents, and has found acceptance in the manufacture of self-polishing floor waxes, insecticidal emulsions, waterless hand cleaners, etc. The wax films can be readily removed by a hot detergent solution, although they are resistant to cold water. One outstanding feature of these soaps is that AMP does not cause yellowing.

AMP is used to adjust the pH of emulsion paints. Such paints, after addition of pigments and modifiers, usually require pH adjustment for good storage stability.

The superior odor of AMP has made it widely accepted for this purpose. AMP has also been shown to be a very good emulsifying agent for these paints.

AMP is used to neutralize alkyd resins intended for aqueous dispersion. Such resins usually have a high acid number which tends to result in gelling. A neutralizing agent will improve storability, but most such compounds remain in the film after baking and make it water sensitive. AMP, however, reacts with the acidic resins during the baking process, forming oxazolines, which are insoluble and water-resistant. The hydrochloride of AMP is used as an acidic catalyst for curing resins applied to textiles (19).

2-Amino-2-methyl-1,3-propanediol. The crystalline grade of this material is used primarily in the preparation of cosmetic creams and lotions as the emulsifying agent in the form of the stearic acid soap (10). Emulsions prepared with it show excellent stability, and one of its salient features is that there is no tendency for yellowing.

Like AMP, this compound is of value as a heat-convertible neutralizing agent for water-dispersible alkyds.

AMPD is used as a raw material for the synthesis of an oil-soluble, cationic, surface-active agent marketed under the trademark Alkaterage-C (Commercial Solvents Corporation).

2-Amino-2-ethyl-1,3-propanediol. This chemical is very similar to AMPD and shares in many of its applications, although it is slightly higher priced on an equivalent weight basis.

Tris(hydroxymethyl)aminomethane. The similarity in structure of Tris Amino to pentaerythritol has led a number of investigators to attempt to use it for alkyd resin synthesis. With its two replaceable amino hydrogen atoms and three hydroxy groups, it would be expected to demonstrate a functionality of five, which should yield unusually hard, tough, and fast-drying resins.

However, because of the ease of formation of the oxazoline (functionality of three), laboratory procedures have yielded products with a functionality of approximately 3.25 instead of the theoretical 5. Furthermore, there is a tendency to form the imide with phthalic anhydride which reduces functionality needed for crosslinking. However, this is not the case with isophthalic acid, and very good products can be made with it.

Despite these difficulties, Tris Amino has been found to be an excellent modifier for alkyd resins if it replaces about 10% of the polyol and if it is added at the end of the cook. This modification has yielded improvements in acid resistance, salt spray resistance, and gloss retention.

It has been known for a number of years that Tris Amino can be used for the preparation of drying-oil vehicles (12), but such products are just beginning to be employed commercially. The objective is to up-grade certain natural oils, which either do not dry properly alone or at best yield inferior films, to give oils which behave similarly to tung and linseed oils, which have long been the standard of the industry. Heretofore, all oils suitable for coatings have been susceptible to attack by micro-organisms, and the addition of bactericides has not been completely satisfactory. It has recently been discovered in laboratory tests and in limited outdoor exposure tests that coatings based on Tris Amino vehicles do not support the growth of molds and fungi which cause mildew. Long-term studies are now under way, and if the

preliminary results are confirmed, a basic weakness of oil-based, or oil-modified, coatings will have been eliminated.

These vehicles can be easily emulsified, can dry rapidly, show good wetting properties, and adhere well to the substrate. They also have good chemical resistance, acid acceptance, and good gloss retention on exposure.

These drying oils are relatively easy to manufacture, as described in connection with oxazolines under Chemical properties.

Tris Amino has several other interesting applications, although of lesser economic importance than the manufacture of protective coatings. When pure, it is a reliable acidimetric primary standard, thus solving an annoying problem for analytical chemists. It is also used as a raw material for the manufacture of demulsifiers for the petroleum industry.

Tris Amino reacts with mineral acids to form salts which have good buffering capacity. It is commonly employed in this use for microbiological purposes since it is relatively nontoxic. It has also been found useful in the transport of live fish, because it can be added to the water to neutralize the carbon dioxide (14).

Nahas and others are investigating the possible use of this product in medicine. It is a relatively nontoxic amine which can be injected into the blood stream to counteract CO₂-induced acidosis resulting from a variety of causes (16).

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ALKOXIDES, METAL

The metal alkoxides are compounds in which a metal is attached to an alkyl group through oxygen. They can be regarded as derived from alcohols by replacement of the hydroxyl hydrogen with a metal, as in NaOCH_3 , $\text{Mg}(\text{OCH}_3)_2$, $\text{Al}(\text{OC}_3\text{H}_7)_3$, and $\text{Ti}(\text{OC}_3\text{H}_7)_4$. Several of these compounds have attained considerable commercial importance in recent years.

The corresponding alkoxides of nonmetals, such as boron and silicon, are discussed under Boron compounds, Silicon compounds, etc. Compounds in which an alkyl group is bound directly to a metal are discussed in such articles as Aluminum compounds, Tin compounds.

Nomenclature. The history of metal alkoxides dates back to the discovery of sodium ethoxide by Liebig in 1837 (1) and the nomenclature reflects this long history. Many of the compounds in this class were originally named as derivatives of the inorganic acid—for example, tetraisopropyl titanate, $\text{Ti}(\text{OPri})_4$. However, the terms “metal alkoxides” and “metal alcoholates” have also been used for many years. In general, modern terminology favors “metal alkoxides,” although the other two are still widely used commercially.

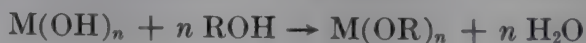
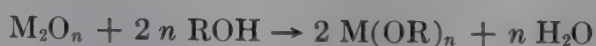
Preparation

There are various methods available for the preparation of metal alkoxides, the simplest of which is the reaction between the metal and alcohol:



This reaction is confined to the alkali metals and magnesium and aluminum; the latter two require catalysts, iodine and mercuric chloride, respectively, or the metal alkoxide itself, to initiate the reaction. Although the reaction proceeds uncatalyzed with the alkali metals, the reactivity of the metal depends on its electropositivity; potassium, for example, combines more readily than sodium. The length of the alkyl group also plays a prominent part; the larger the group the slower the reaction, because of the reduced acidity of the hydroxylic hydrogen atom. Thus, butanol reacts less rapidly with sodium than do either methanol or ethanol.

A second method of preparation involves reaction between the metal oxide or hydroxide and alcohol:

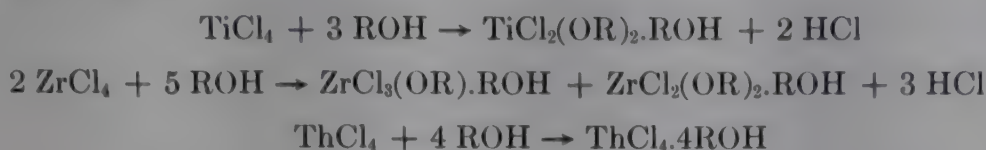


These reactions are reversible and for them to go to completion it is necessary to remove the water as it is formed. Sodium ethoxide may be produced from sodium hydroxide and ethanol by azeotropic dehydration using benzene. While this method is also confined mainly to the strongly electropositive elements, vanadyl alkoxides, $\text{VO}(\text{OR})_3$, have been obtained by treatment of vanadium pentoxide with alcohols (2).

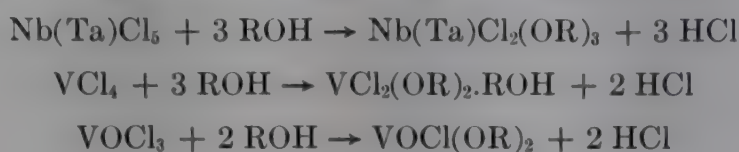
The behavior of thallium is noteworthy. Lamy (3) found that the metal does not react when suspended in boiling ethanol, but a piece held in air over the surface of the alcohol reacts readily. The metal first oxidizes in air and the oxide then reacts with the alcohol as shown above. The insolubility of thallous ethoxide in ethanol favors its formation.

For the preparation of alkoxides of the less electropositive elements, the metal chlorides are convenient starting materials. In no case does the direct reaction

between the chloride and alcohol give the fully substituted alkoxide; chloroalkoxides or addition compounds are formed. With the tetrachlorides of the group IVA metals, for example, the degree of substitution decreases with increase in atomic number of the central atom (4–6):



Of the group VA metals, the pentachlorides of tantalum and niobium undergo trisubstitution, whereas vanadium tetrachloride and oxytrichloride resemble titanium tetrachloride in that disubstitution takes place exclusively (7–9):

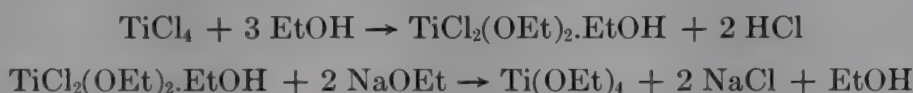


Molybdenum pentachloride also undergoes disubstitution (8):



Most other metal chlorides form only addition products of the type $\text{MCl}_n.x\text{ROH}$. Examples are $\text{SnCl}_4.2\text{ROH}$; $\text{MnCl}_2.\text{ROH}$; $\text{ZnCl}_2.2\text{ROH}$; etc.

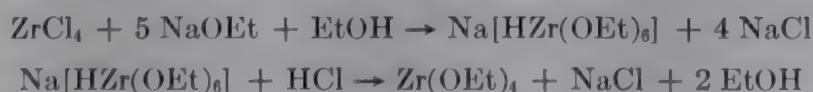
Although the replacement of chlorine is not complete in these substitution reactions, the partial replacement occurs very rapidly and exothermically. Prolonged treatment of the resultant metal chloride–alkoxide with an excess of boiling alcohol fails to cause further reaction. In order to prepare the fully substituted alkoxide, it is necessary to employ a base to cause further replacement of chlorine. In 1924 Bischoff and Adkins (10) prepared titanium tetraethoxide from the reaction between titanium tetrachloride, ethanol, and sodium ethoxide:



This method now has wide applicability, and in general may be used with all but the most ionic metal chlorides; a notable exception is zirconium tetrachloride. Gilman and co-workers (11) have introduced a modification of this method for the preparation of insoluble alkoxides. They prepared uranium tetramethoxide by reaction between uranium tetrachloride and lithium methoxide in methanol; the product was separated by filtration from the methanolic solution of lithium chloride:

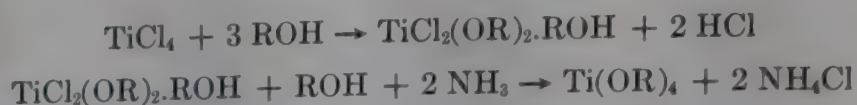


A similar method was used by Bradley and co-workers in the preparation of lanthanum trimethoxide (12) and uranyl methoxide (13), both of which are insoluble. Meerwein and Bersin (14) found that zirconium tetraalkoxides could not be obtained by the sodium alkoxide method because of the formation of stable double alkoxides. They report that the acid sodium zirconium ethoxide $\text{Na}[\text{HZr}(\text{OEt})_6]$ was produced from zirconium tetrachloride and sodium ethoxide in ethanol, and that the tetraalkoxide could be obtained only by the action of an equivalent amount of ethanolic hydrogen chloride:



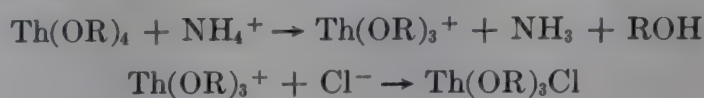
These results conflict with those of Bradley (15) who agrees, however, that a double complex prohibits the isolation of zirconium tetraethoxide.

More recent work has shown that anhydrous ammonia may be used instead of sodium ethoxide; thus Nelles (16) prepared titanium alkoxides from the reaction of titanium tetrachloride, alcohol, and ammonia. Numerous other workers have since repeated this.



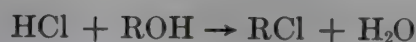
Trialkoxides of iron (17), tetraalkoxides of zirconium (15,18), hafnium (19), and germanium (20), and pentaalkoxides of niobium (21,22) and tantalum (23,24) have also been prepared directly from the chlorides by this method.

The ammonia method failed to produce a chloride-free product in attempts to prepare thorium tetraalkoxides from the tetrachloride (25). This was due to thorium alkoxides being stronger bases than ammonia in alcoholic solution:



Fortunately the sodium method is satisfactory in this case, no doubt because of the stronger basicity of the alkoxide ion relative to the thorium alkoxide.

In all these reactions, the alkyl group can play an important part. For example, reactions involving alcohols containing an electron-releasing alkyl group, such as *t*-butyl alcohol, lead to the formation of a hydrolyzed product. This is due to a secondary reaction between the alcohol and hydrogen chloride to give an alkyl chloride and water:



Methods of suppressing this side reaction have been found, and Cullinane et al. (26,27) have shown that the presence of a base (such as pyridine) with the tertiary alcohol was essential in the preparation of titanium tetra-*t*-butoxide from titanium tetrachloride. The base acts as an acid acceptor and removes hydrogen chloride as it is formed. It has also been shown that dipyridinium hexachlorozirconate, $(\text{C}_5\text{H}_5\text{N})_2\text{ZrCl}_6$ is a better starting material than the tetrachloride for the preparation of zirconium alkoxides (28). Another pyridine complex that has been used with the sodium alkoxide method is that of thorium $(\text{C}_5\text{H}_5\text{N})_2\text{ThCl}_6$ (25). Pyridine complexes that have been used with the ammonia method are those of uranium, $(\text{C}_5\text{H}_5\text{N})_2\text{UOCl}_5$ (29), plutonium, $(\text{C}_5\text{H}_5\text{N})_2\text{PuCl}_6$ (30), and cerium, $(\text{C}_5\text{H}_5\text{N})_2\text{CeCl}_6$ (31). The plutonium and cerium complexes are especially advantageous because plutonium and cerium tetrachlorides are unknown.

Another method of preparation involves the reaction between the metal dialkylamide and alcohol. This was first used by Gilman et al. (11) who prepared uranium tetraalkoxides from tetrakisdiethylamino uranium, $\text{U}(\text{NEt}_2)_4$, and was later developed by Thomas (32) to cover the preparation of alkoxides of titanium, zirconium, vanadium (IV), niobium, tantalum, and tin:



This reaction proceeds at room temperature in nearly quantitative yield and no complications are introduced with by-product formation. The method is particularly suitable for the preparation of stannic alkoxides, and also is the only method mild enough

for the preparation of the relatively unstable niobium penta-*t*-alkoxides and vanadium (IV) tetraalkoxides. Another advantage is that only the theoretical quantity of alcohol is required. This may be of use when the alcohol is hard to obtain or too reactive, as in the unsaturated or higher tertiary alcohols where the usual excess would lead to by-product formation.

The so-called "alcohol interchange" reaction provides a means of converting one metal alkoxide to another of the same metal:



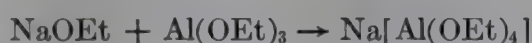
This equilibrium appears to be present with most alkoxides in alcoholic solution, and by a suitable choice of the group R the new alkoxide, $M(OR')_n$, may be obtained in quantitative yield. It is convenient to start with a lower alkoxide, $M(OR)_n$, so that fractional distillation provides a means of removing the lower alcohol, ROH; however, by using a large excess of the lower alcohol, a lower alkoxide can be obtained from a higher one. The formation of methoxides or ethoxides is sometimes facilitated by insolubility.

An analogous method, discovered by Mehrotra (33), is a transesterification process using an alkyl ester and metal alkoxide:



Although this reaction does not, in general, proceed quite as readily as the alcohol-interchange reaction, the same principles apply in its application.

Double Alkoxides. Alcoholic solutions of the alkoxides of aluminum, titanium, zirconium, iron(III), tin(IV), and uranium are acidic and may be titrated under anhydrous conditions to a sharp end point with alkali-metal or alkaline-earth-metal alkoxides, which are basic. Thymolphthalein is used as indicator and the so-called double alkoxides are obtained:



Meerwein and Bersin (14) prepared and investigated over fifty of these compounds and considered them to be "alkoxy salts" in which the more electropositive metal became the cation and the other metal became the central atom in the anion, as $Na[Fe(OEt)_4]$, $Li[Al(OMe)_4]$. However, there is very little physical evidence for regarding these compounds as salts even though they are obtained from an acid-base reaction; their solubility in organic solvents and in many cases their volatility suggest that they are covalent rather than ionic and are best termed "double alkoxides."

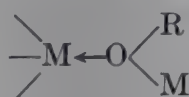
Physical Properties

The metal alkoxides show an exceptional gradation in physical properties. These range from the solid nonvolatile compounds of the strongly electropositive metals through the polymeric covalent compounds of low volatility of the heavier multivalent elements to the volatile monomeric covalent liquids of the lighter transition elements.

Little work has been carried out on the physical properties of the alkali metal alkoxides. Their thermal stability, solubility in alcohols, and nonvolatility indicate that they are probably ionic, and conductance measurements with dilute ethanolic solutions of sodium ethoxide support this conclusion (34).

Magnesium alkoxides are also nonvolatile and thermally stable. Magnesium methoxide is prepared in methanol, in which it remains soluble up to 5%, or supersaturated up to 8–10%. It can be obtained from this solution as crystals containing alcohol of crystallization. On driving off the alcohol, however, the resulting powder is insoluble in methanol, which suggests that pure magnesium methoxide is either a giant covalent molecule or an ionic molecule with a high lattice energy. However, there is no doubt as to the covalent nature of aluminum alkoxides; the polymeric aluminum ethoxide has negligible specific conductance in the fused state over a wide temperature range (35) and even the insoluble solid methoxide is volatile and may be sublimed in a molecular still at 240°C (36).

An extensive study of the covalent alkoxides of the transition metals has been carried out by Bradley and co-workers over the last ten years, and it was found that the polymeric nature of many of these compounds is due to the covalency expansion of the metal, involving intermolecular bonds with oxygen from neighboring alkoxide groups:



Molecular weight measurements on a large number of alkoxides indicate that steric factors play a prominent part, and the metal atom can be hindered from covalency expansion by surrounding bulky alkoxy groups. The greater the degree of branching of the alkyl group, the greater the shielding. Thus, the molecular complexity of *t*-butoxides is always less than that of the *n*-butoxides. In addition, for metals of the same valence the shielding requirements are governed by the atomic radius of the metal atom, and the smaller the metal atom the smaller is the alkyl group required to shield it completely. For example, with the group IVA metals, the smallest alkoxide groups to give monomeric tetraalkoxides are: Ti, —OPrⁱ; Zr(Hf), —OBu^t; Ce, —OCMeEt₂; Th, —OCeEt₃.

Complete summaries of this work are given in the reviews by Wardlaw (37,38) and Bradley (39,40). In addition, a structural theory on this subject has been put forward by Bradley (41), which may briefly be summarized by stating that metal alkoxides may undergo the minimum degree of polymerization consistent with the maximum covalency of the metal. Cryoscopic measurements on titanium ethoxide in benzene (42) indicated that the degree of polymerization increased to a limiting trimeric

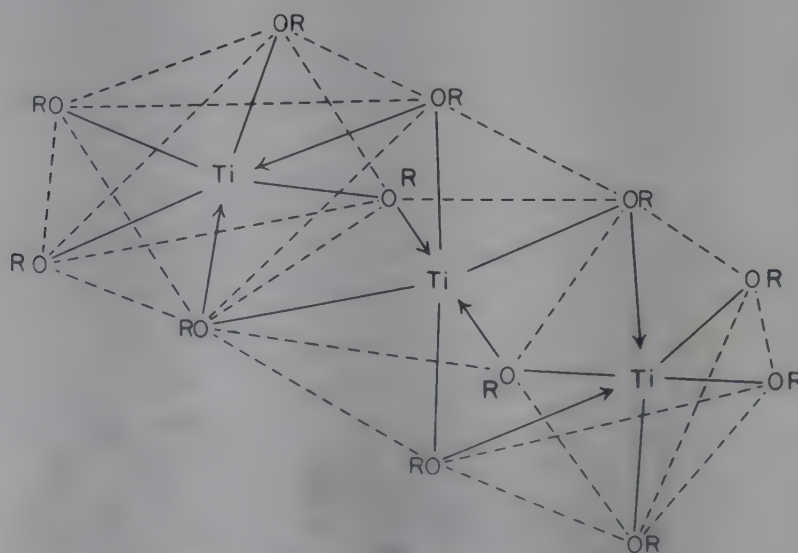
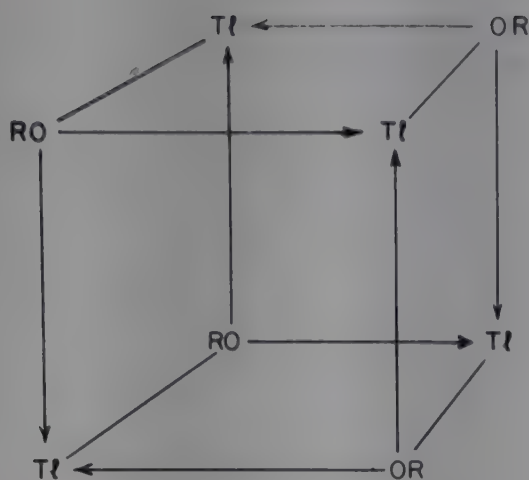
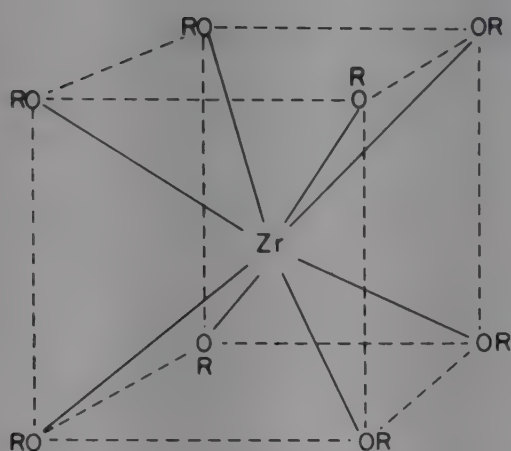
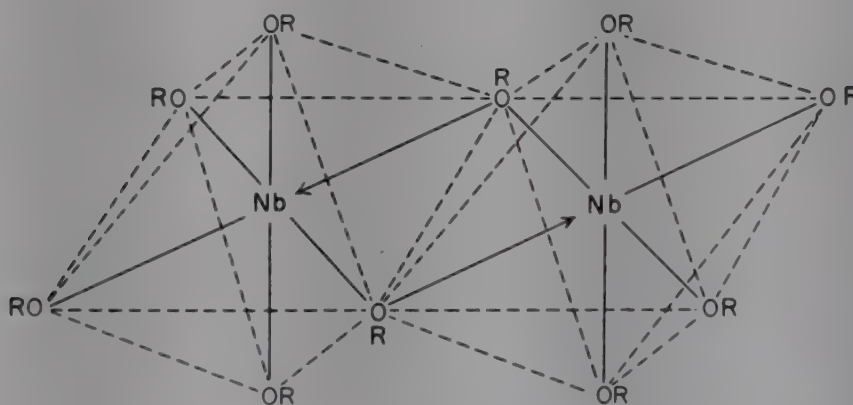


Fig. 1. Structure of Ti₃(OR)₁₂.

Fig. 2. Structure of $Tl_4(OR)_4$.Fig. 3. Structure of $Zr(OR)_8$. Left, unit A; right, plan view, eight of unit A.Fig. 4. Structure of $Nb_2(OR)_{10}$.

state in which each titanium atom was exhibiting its maximum covalency of six. The titanium atom in this case may be considered to be in the center of a regular octahedron with alkoxy groups at each corner. The trimeric structure then consists of three octahedra connected across faces, as in Figure 1.

Other examples may be cited: Thallous alkoxides, in contrast to those of the alkali metals, are never more than tetrameric (maximum covalency 3, cubic structure Fig. 2); alkoxides of zirconium, cerium, hafnium, and thorium are never more than octameric (maximum covalency 8, cubic structure Fig. 3); and niobium and tantalum alkoxides are never more than dimeric (maximum covalency 6, octahedral structure Fig. 4). In the case of a bivalent metal with a maximum covalency of six,

such as magnesium, this theory indicates that an infinite polymer is the smallest consistent with the metal exhibiting its maximum covalency.

The case of aluminum is interesting. This metal has a maximum covalency of six but has a tendency to exhibit a covalency of four; the former results in an octamer as the smallest polymer and the latter a dimer. Mehrotra (43) has found that aluminum isopropoxide is dimeric in the vapor state, trimeric immediately after distillation, and tetrameric after storage for several months. Other authors (44) give values between five and six for the degree of polymerization of this compound. Thus, it would seem that the metal initially exhibits a covalency of four, giving a dimer, but this changes slowly on standing. An "ageing" effect takes place. This rearrangement in the solid state at room temperature is obviously slow; therefore the degree of polymerization of this alkoxide depends on its past history. The steric effect of the *t*-butoxy group is such that aluminum *t*-butoxide is dimeric at all times (43).

The volatilities of metal alkoxides are of course greatly affected by the degree of polymerization, and Table 1, which lists results obtained by Bradley and co-workers

Table 1. Boiling Points and Molecular Complexities of Titanium and Zirconium Amyloxides

R in M(OR) ₄	Titanium alkoxide		Zirconium alkoxide	
	Bp, °C/mm	Molecular complexity	Bp, °C/mm	Molecular complexity
—CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	175/0.8	1.4	256/0.01	3.2
—CH ₂ CH ₂ CH(CH ₃) ₂	148/0.1	1.2	247/0.1	3.3
—CH ₂ CH(CH ₃)CH ₂ CH ₃	154/0.5	1.1	238/0.1	3.7
—CH ₂ C(CH ₃) ₃	105/0.05	1.3	188/0.2	2.4
—CH(CH ₂ CH ₃) ₂	112/0.05	1.0	178/0.05	2.0
—CH(CH ₃)CH ₂ CH ₂ CH ₃	135/1.0	1.0	175/0.05	2.0
—CH(CH ₃)CH(CH ₃) ₂	131/0.5	1.0	156/0.01	2.0
—C(CH ₃) ₂ CH ₂ CH ₃	98/0.1	1.0	95/0.1	1.0

(45) on the volatilities and molecular complexities of titanium and zirconium amyloxides, serves to illustrate this. It is also a good example of the effect of branching of the alkyl group on molecular complexity and the smaller shielding requirements of the titanium atom in comparison with the larger zirconium atom. In certain cases, with a series of monomeric alkoxides of metals of the same group, those with the highest molecular weight are the most volatile. The boiling points of the *t*-amyloxides of titanium, zirconium, and hafnium decrease in that order. The difference is not large but definitely outside the range of experimental error. A theoretical interpretation of this has been put forward by Bradley (46) and involves equalization of intermolecular attraction because of the shielding of the central metal atom by the surrounding alkoxy groups. This effect is also shown by the similarity in boiling points of monomeric alkoxides with approximately the same number of carbon and hydrogen atoms—for example, tantalum penta-*t*-butoxide, TaO₅C₂₀H₄₅, bp 149.5°C at 5.5 mm; and titanium tetra-*t*-amyloxide, TiO₄C₂₀H₄₄, bp 143°C at 5.0 mm.

The physical properties of some representative alkoxides are given in Table 2, and those of some double alkoxides in Table 3. Under melting points, "decomp" before °C indicates decomposition without melting at °C, and "decomp" after °C indicates decomposition with melting at °C.

Table 2. Physical Properties of Alkoxides

Alkoxide	Nature	Mp, °C	Bp, °C/mm	Solubility		Refer- ence
				ROH ^a	Org solv	
LiOEt	white solid			cryst	sol	64
NaOEt	white solid	decomp 260		sol	insol	64
KOEt	white solid			sol	insol	64
TlOMe	white solid	decomp 120		insol	insol	64
TlOAm ^t	white solid	decomp 50		cryst	sol	65
Mg(OEt) ₂	white solid			cryst	mod sol	64
Ca(OEt) ₂	white solid			sol	insol	64
Sr(OEt) ₂	white solid			sol	insol	64
Ba(OEt) ₂	white solid	decomp 230		sol	insol	64
Zn(OEt) ₂	white solid			insol	insol	64
Pb(OEt) ₂	white solid			insol	insol	64
Al(OEt) ₃	white solid	150–160	175/3	sol	sol	64
Al(OPr ⁱ) ₃	white solid	118	124/3	sol	sol	66
La(OMe) ₃	white solid		>360/10 ^{−4}	insol	insol	36
La(Obu ^t) ₃	white solid		subl 280/10 ^{−4}	sol	cryst ^b	36
Fe(OEt) ₃	dark-brown solid	120	155/0.1	cryst	sol	17
Fe(OPr ⁱ) ₃	dark-brown solid		subl 149/0.1	sol	sol	17
Cr(OEt) ₃	dark-green solid			cryst		64
Ti(OEt) ₄	white solid	100	103/0.1	sol	sol	56
Ti(OPr ⁱ) ₄	colorless liquid		97/7.5	sol	sol	56
Zr(OEt) ₄	white solid	171–173	180/0.1	sl sol	sol	28
Zr(OPr ⁱ) ₄	white solid	105–120	160/0.1	cryst	sol	15
Hf(OEt) ₄	white solid	170	180/0.1	sl sol	sol	19
Hf(OPr ⁱ) ₄	white solid	110	160/0.1	cryst	sol	19
Ce(OEt) ₄	yellow solid	200 decomp		insol	insol	31
Ce(OPr ⁱ) ₄	yellow solid		subl 160–170/0.05	mod sol	sol	67
Th(OEt) ₄	white solid		decomp 300/0.05	insol	insol	25
Th(OPr ⁱ) ₄	white solid	110	200/0.05	mod sol	sol	25
Ge(OEt) ₄	colorless liquid		54.4/5.0	sol	sol	68
Ge(OPr ⁱ) ₄	colorless liquid		82/5.0	sol	sol	68
Sn(OEt) ₄	white solid		decomp 175/0.05	sol	sol	69
Sn(OPr ⁱ) ₄	white solid		131/1.6	cryst	sol	69
V(OPr ⁱ) ₄	dark-green solid	40	55/0.1	sol	sol	32
V(Obu ^t) ₄	royal-blue liquid		55/0.05	sol	sol	32
Cr(Obu ^t) ₄	blue solid	37–38	105/15	sol	sol	70
U(OEt) ₄	green solid		decomp	sl sol	insol in Et ₂ O	11
U(Obu ^t) ₄	green solid			sol	sol	11
Pu(OPr ⁱ) ₄ .-						
Pr ⁱ OH	green solid		subl 220/0.05	cryst	sol	30
Pu(Obu ^t) ₄	green solid		subl 112/0.05	sol	sol	30
VO(OEt) ₃	yellow liquid		108/26	sol	sol	2
VO(Bu ^t) ₃	white solid	45–47	117/15	sol	sol	2
Nb(OEt) ₅	pale-yellow liquid		156/0.05	sol	sol	21
Nb(OPr ⁱ) ₅	white solid		subl 60–80/0.1	cryst	sol	21
Ta(OEt) ₅	colorless liquid		147/0.2	sol	sol	26
Ta(OPr ⁱ) ₅	white solid	84	122/0.1	sol	sol	24
U(OEt) ₆	dark-brown liquid		160/0.05	sol	sol	29, 55
U(OPr ⁱ) ₅	golden solid	320 decomp	subl 160/0.01	sol	sol	29, 55
U(OEt) ₆	dark-red liquid		72/0.001	sol	sol	53
U(OPr ⁱ) ₆	dark-red solid	167–168	subl 135/0.004	sol	sol	53

^a In this column “cryst” indicates that the alkoxide may be crystallized from alcohol.
^b Crystallizes from a mixture of benzene and petroleum ether.

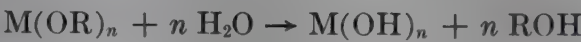
Table 3. Physical Properties of Double Alkoxides

Alkoxides	Nature	Mp, °C	Bp, °C/mm	Solubility		Refer- ence
				ROH ^a	Org solv	
K[Li(OPr ⁱ) ₂]	white solid			cryst		14
Na[Zr ₂ (OPr ⁱ) ₉]	white solid	168–180	260/1	sol	sol	72
K[Zr ₂ (OPr ⁱ) ₉]	white solid		subl 200/0.2	sol	sol	72
Li[Zr ₂ (OEt) ₉]	white solid		260/0.2	sol	cryst in benzene	72
Tl[Zr ₂ (OPr ⁱ) ₉]	white solid		subl 220/0.5	cryst		72
Mg[Al(OEt) ₄] ₂	white solid	129	220–228/4	sol		14
Ca[Al(OPr ⁱ) ₄] ₂	white solid	124	230–240/3	sol		14
K[Al(OBu ^t) ₄]	white solid	164–165		sol		14
Mg[Al(OPr ⁱ) ₄]	white solid	20	130–142/2	sol		14
Co[Al(OEt) ₄] ₂	violet solid			sol	sol	14
Na[Sn ₂ (OEt) ₉]	white solid	decomp 260		cryst	sol	73
Ca[U(OEt) ₆] ₂	light-green solid		subl 200/0.001	sol	insol in petroleum ether	52
Al[U(OEt) ₆] ₃	green liquid		111–115/0.0012	sol	sol	52
U[Al(OPr ⁱ) ₄] ₄	green oil		95–97/0.001	sol	sol	74
Na[U(OEt) ₆]	green solid	decomp on heating		sol	sl sol	52

^a In this column “cryst” indicates that the alkoxide may be crystallized from alcohol.

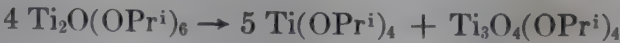
Chemical Properties

The most notable property of metal alkoxides is their ease of hydrolysis to the metal hydroxides or hydrated oxides. This necessitates the handling of these compounds in the absence of moisture.



The reversibility of this reaction with the strongly electropositive metals has already been noted (see p. 832); with the covalent multivalent metal alkoxides, however, the reaction is irreversible.

Studies of the hydrolysis of titanium and zirconium alkoxides are summarized by Bradley (39,40). Low-molecular-weight polymers are formed in the early stages of hydrolysis, and these tend to disproportionate on heating to regenerate the volatile tetraalkoxide and leave a more highly polymerized nonvolatile residue.

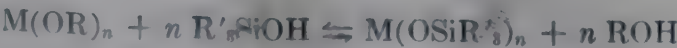


The rapidity and completeness of hydrolysis depend on the size of the alkyl group; hydrolysis is slower and less complete the higher the alkyl group. Results in this field have provided useful data on the structural elucidation of these alkoxides.

Metal alkoxides also react with other compounds containing hydroxyl groups and, besides the ready alcohol-interchange reaction previously mentioned, phenolic compounds react to give metal phenoxide derivatives:



Trialkylsilanols also react to give the corresponding trialkylsilyloxy-metal derivatives (47).



This reaction is similar to the alcohol-interchange reaction but is complicated by two side reactions that can take place. Metal alkoxides catalyze the self-condensation of the lower trialkylsilanols to hexaalkyldisiloxanes and water, and trialkylsilanols react with alcohols to give alkoxysilanes and water; the water in each case causes hydrolysis of the product. These side reactions may be eliminated by the slow addition of the silanol to the alkoxide in an inert solvent with the simultaneous removal of the liberated alcohol by distillation. Trialkylsilyloxy compounds of titanium, zirconium, niobium, and tantalum have been obtained by this method.

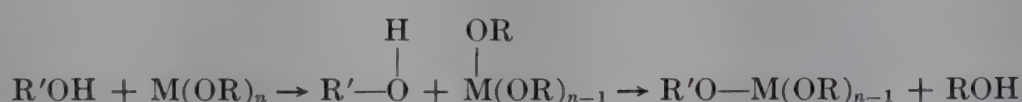
Organic acids react to give the metal salts:



As might be expected, reaction occurs most readily with the strongly basic alkoxides of the more electropositive metals. Mehrotra (48) found that with titanium tetraalkoxides it was not possible to obtain tetrasubstituted derivatives; products of the type $[(R'COO)_3Ti]_2O$ were obtained with acetic, butyric, valeric, and palmitic acids. This was attributed to steric factors and was confirmed by the discovery that zirconium tetraethoxide and acetic acid gave the fully substituted tetraacetate (49). Zirconium is a larger atom than titanium and is able to accommodate four bulky surrounding acid groups (see Physical properties).

Reagents which can enolize also react; β -diketones give a tetrachelate derivative with zirconium tetraalkoxides, in which the metal exhibits its maximum covalency of eight. Titanium alkoxides, however, because of the covalency maximum of six for titanium, give bisalkoxy-bischelate derivatives only. Chelate compounds are also formed with reagents such as 8-hydroxyquinoline.

It is perhaps surprising that no reaction takes place with mercaptans to form metal mercaptides, although the thiol hydrogen atom is more acidic than the alcoholic hydroxyl hydrogen atom. Bradley (39) states that the electron donor power of the atom adjacent to the active hydrogen atom (namely, the oxygen or sulfur atom) is important because these reactions may well be initiated by a coordination mechanism:



Ineffective coordination between sulfur and metal would then account for this lack of reactivity. In addition, alkylamines do not undergo substitution reactions with metal alkoxides to give alkylamino derivatives, although Cook (50) has reported the formation of a weak addition compound between titanium isopropoxide and ethylamine, $Ti(OPr^i)_4 \cdot EtNH_2$. Both metal mercaptides and dialkylamino derivatives react readily with alcohols to give the fully substituted alkoxides.

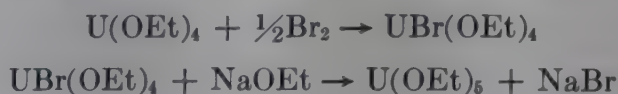
The tendency of metal alkoxides to coordinate with donor molecules is low, and intermolecular coordination is favored; however, a few alcoholates, $Zr(OPr^i)_4 \cdot Pr^iOH$, and pyridine complexes, $Ce(OPr^i)_4 \cdot C_5H_5N$, are known.

Investigation of other chemical properties of alkoxides has mainly been confined to those of aluminum and the transition metals, titanium and zirconium in particular. These compounds, being wholly covalent, undergo numerous reactions not possible with the more ionic derivatives.

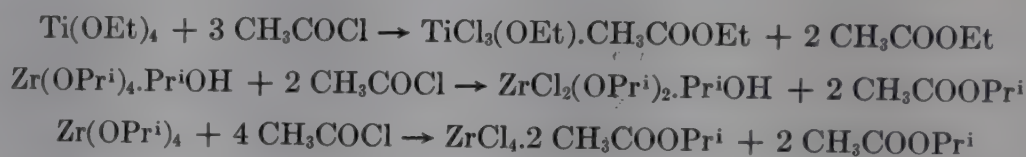
The substitution of halogen for alkoxy groups in metal alkoxides may be carried out in a number of ways. Reaction between anhydrous hydrogen chloride and several

metal alkoxides takes place readily. Mehrotra (51) has shown that titanium and zirconium give products identical to those obtained in the reactions between the metal chlorides and alcohol (see Preparation, p. 832). Gilman and co-workers (52,53) prepared a series of chloroalkoxides of uranium(V) and uranium(VI) by this method.

Haloalkoxides may also be obtained by reaction of the free halogen with the alkoxide, and Nesmayanov et al. (54) found that titanium dihalodialkoxides, $\text{TiX}_2(\text{OR})_2 \cdot \text{ROH}$, could be obtained by the reaction of chlorine or bromine with titanium alkoxides. In contrast, Gilman et al. (55) discovered that bromine oxidized uranium(IV) tetraethoxide, with no substitution, and formed uranium(V) monobromotetraethoxide. Reaction of this product with sodium ethoxide gave the pentaethoxide of uranium:



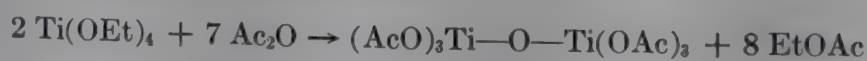
The reactions between acetyl chloride and metal alkoxides also give chloroalkoxides, and various degrees of substitution may be obtained depending on the molar ratios of reactants used. Bradley and co-workers (5,56) have carried out a series of reactions of this type with titanium and zirconium alkoxides. In several cases, strong addition complexes were formed between the product and alkyl acetate formed during the reaction. When alkoxide alcohol addition compounds were used, no hydrogen chloride was liberated from a secondary reaction.



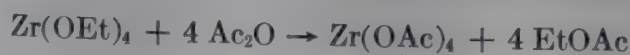
Interchange reactions between metal chlorides and metal alkoxides give chloroalkoxides; thus an excess of titanium tetrachloride and titanium tetraalkoxides gives trichloride monoalkoxides of titanium (56):



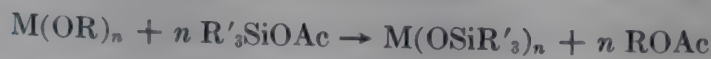
Mehrotra (57) found that acetic anhydride reacted with titanium ethoxide to give hexaacetoxydititanoxane and ethyl acetate:



This is the same product that was obtained with acetic acid and, as before, steric factors were assumed to be the cause of the failure to obtain the tetraacetate. The same author prepared zirconium tetraacetate by a similar method:



Trialkylsilyl acetates react to give the metal trialkylsilyloxy derivatives (47).



This reaction is similar to the transesterification reaction (see Preparation) but is irreversible. The reaction is also much slower and the rate decreases with increase in size of the alkyl group R' . In addition, reactions in which trimethylsilyl acetate is a reagent may be accompanied by a side reaction causing the formation of metal oxyacetates; this reduces the yields in several cases. There is no tendency for acetylation with the higher trialkylsilyl acetates. Trialkylsilyloxy derivatives of titanium, zirconium, and tantalum have been prepared by this method.

Although most of the last few reactions described have been investigated for the alkoxides of only a few metals, it should be stated at this stage that there seems no reason to doubt that similar reactions would take place with the covalent alkoxides of other metals, such as niobium, tantalum, tin, vanadium, vanadyl, etc.

Metal alkoxides have fairly wide use in organic chemistry, and the reactions with carbonyl compounds are perhaps the most important. The Tishchenko reaction (58) involves the conversion of an aldehyde to an ester:

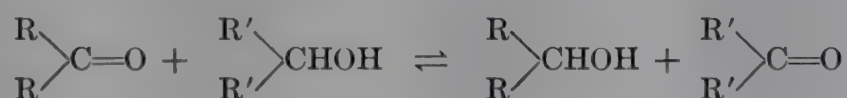


Aluminum alkoxides were found to be the most effective catalysts, and a few mole percent was all that was required to give high yields. More recent work on this reaction (59,60) has revealed that more basic alkoxides, such as $\text{Mg}(\text{OEt})_2$, cause the aldehyde to undergo an aldol condensation initially; this is then followed by a crossed Tischchenko reaction between the aldol and the original aldehyde.



The strongly basic sodium alkoxides produce only an aldol condensation. Benzaldehyde, which contains no α -hydrogen atom, cannot undergo an aldol-type condensation; with sodium hydroxide the normal Tishchenko reaction takes place and benzyl benzoate is formed (61).

Another reaction which has been the subject of much study is the Meerwein-Ponndorf-Oppenauer oxidation reduction. This reaction involves the conversion of ketones to secondary alcohols, or vice versa:



Alkoxides of sodium and magnesium were initially used as catalysts for this reaction but it was later shown that alkoxides of aluminum, zirconium, tin(IV), titanium, antimony, or iron could also be used (62). The latter are less inclined to cause alternative condensation reactions because of their lower basicity, and aluminum alkoxides are generally favored because of their availability. The large amount of work carried out on the mechanism of this reaction is summarized by Bradley (39,40). There is now no doubt that the reaction proceeds through a cyclic transition stage involving the alkoxide and covalency expansion of the metal.

The ease of covalency expansion of the metal probably accounts for the catalytic behavior of metal alkoxides in organic reactions. Strong evidence for this was obtained by McElvain and others (63), who found that aluminum alkoxides caused conversion of carboxylic orthoesters to ketene acetals:



The ester was assumed to go through a cyclic transition stage involving coordination to the metal in the alkoxide. It was found that the less polymerized aluminum alkoxides, such as *t*-butoxide or isopropoxide, were more effective catalysts than the more highly polymeric methoxide or ethoxide.

Analytical Methods

The ease of hydrolysis of metal alkoxides makes metal analysis of these compounds a comparatively simple task. In many cases, the metal may be estimated by straight hydrolysis of a sample in a crucible, and ignition to the metal oxide. Alternatively, the metal may be brought into solution by hydrolysis of a sample with dilute acid, followed by a standard analytical procedure for a solution of that particular metal. If the alcohol liberated during the hydrolysis is likely to cause interference, it may be distilled from the solution by boiling.

The estimation of alkoxy groups is not such a simple task. Bradley and co-workers (5,15) have developed a method for certain alkoxy groups, which involves hydrolysis and oxidation of the liberated alcohol with excess standard potassium dichromate solution. The excess may then be estimated iodometrically. This method is suitable only for methoxides, ethoxides, and isopropoxides; quantitative conversion to carbon dioxide, acetic acid, and acetone, respectively, takes place. An alternative method for ethoxides is oxidation followed by distillation, and titration of the liberated acetic acid.

For higher alkoxy groups, standard carbon and hydrogen analysis may be used, although careful sample preparation is required because of the ease of hydrolysis. Quantitative vapor phase chromatography of alcohol liberated during hydrolysis may also be used, but care must be taken in this case to insure that hydrolysis is complete before the estimation is carried out.

Manufacture, Economic Aspects, and Applications

Commercial manufacture of the metal alkoxides follows textbook preparation methods, but a good deal of know-how and rigid adherence to optimum conditions are necessary to obtain economic yields. Although many metal alkoxides are available in laboratory, pilot plant or semicommercial quantities, only the following have obtained full commercial stature.

Aluminum Isopropoxide (aluminum isopropylate), $(\text{Al}(\text{OPr}^i)_3)_x$, is a white solid in its associated state. The melting point of commercial material varies from 118.5°C to about 138°C; boiling point, 135°C at 10 mm. The most usual method of manufacture is by direct reaction of aluminum and isopropyl alcohol. In one procedure, aluminum ingots are dissolved in excess isopropyl alcohol, using mercuric chloride or iodine as catalyst, stripping off the excess isopropyl alcohol and distilling off the remaining aluminum isopropoxide. This process has been greatly improved in a recent patent (71). The new procedure ideally controls the reaction, uses no catalysts, and gives nearly quantitative yields. The aluminum is contained in a tower above the isopropyl alcohol and the alcohol is refluxed through the column, continually washing the product into the stillpot until 100% concentration is reached. The product is then drawn off and distilled under vacuum. The stillpot is recharged with alcohol and the process is repeated. This process also lends itself to continuous production by continually drawing off product and feeding in alcohol and aluminum. Aluminum isopropoxide can also be produced by the addition of excess isopropyl alcohol to a benzene solution of aluminum chloride, followed by passage of dry ammonia which precipitates ammonium chloride. The ammonium chloride is filtered off and the isopropoxide is separated by distillation.

Alkoxides of the higher boiling alcohols are usually prepared from the aluminum isopropoxide by heating with the stoichiometric quantity of the desired alcohol and by distilling off the liberated isopropyl alcohol. Aluminum isopropoxide is produced by

Harshaw Chemical Company, Anderson Chemical Division of Stauffer Chemical Company, and Chattam Chemical Company in the United States; by Union Chimique Française, S.A.R.L., in France; by Rhein Preussen, A.G., and Riedel de Haen in Germany; and by Kaylene Chemicals, Ltd., in England. Aluminum isopropoxide is supplied in tins or drums, in fused or granular form. It is sold by Anderson Chemical under the following specifications:

forms available.....	solid or granular
ester, %.....	99.9+ as produced
(This designation, used widely in the chemical industry, refers to percentage of aluminum isopropoxide.)	
molecular weight.....	816.92 (tetrameric form)
boiling point, °C at 10 mm.....	135–138
iron, %.....	0.000

As of October 1961 prices in dollars per pound were as follows:

drums, T/L and C/L.....	0.320
drums, LCL.....	0.325

Although production and sales data for aluminum isopropoxide are not reported by the U.S. Tariff Commission, it is estimated that production in the United States exceeds 1,000,000 pounds. In addition to its use as a selective reducing agent for aldehydes and ketones (see Chemical properties), aluminum isopropoxide has recently found considerably increased use through its application as an intermediate in the manufacture of aluminum glycinate for formulations of antiperspirants, and as a paint additive for removing water from pigments, decreasing wrinkling tendencies, and improving water resistance.

Sodium Methylate (sodium methoxide), NaOCH₃, is a white hygroscopic solid; formula weight 54. Commercial manufacture of this material is either by reaction of molten sodium with methyl alcohol or by the reaction of methyl alcohol with sodium amalgam obtained from the electrolysis of brine in a Castner mercury cell (76). Both these methods produce a solution of sodium methylate in methanol and the product is offered in two forms: a 25% solution in methanol; and a solid, which is a dry, free-flowing white powder obtained by evaporating off the methanol. More recently the direct production of dry sodium methylate has been carried out by the introduction of methanol vapors to molten sodium in a heavy-duty agitating-type reactor. The solid is supplied in polyethylene bags contained in airtight drums filled in a nitrogen atmosphere. The 25% solution is supplied in standard 55-gallon drums, tank cars, or tank trucks. Production of sodium methylate in 1960 was given as 4,088,000 pounds by the U.S. Tariff Commission. The material is presently manufactured by Harshaw Chemical Company, Anderson Chemical Division of Stauffer Chemical Company, and the Chemical Division of the Olin-Mathieson Chemical Corporation in the United States; in Germany by Feldmuehle Papier und Zellstoffe Werke, A.G., and Badische Anilin- und Soda-Fabrik. Typical specifications are given as follows:

Power grade	Composition, %
sodium methylate.....	97.5
sodium hydroxide.....	0.5
sodium carbonate.....	0.4
sodium formate.....	0.3
methanol (free).....	0.5

<i>Liquid grade (25% in methanol)</i>	
sodium methylate content, %	25 minimum
color and form	slightly cloudy to clear colorless solution
density, lb/gal	about 7
initial boiling point, °F	188
flash point, °F (Cleveland open cup)	85-90
flash point, °F (closed cup)	80
crystallization temp, °F (after equilibrium)	30

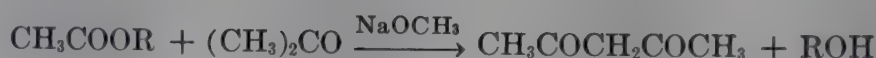
In October 1961, prices in dollars per pound were as follows:

	<i>Liquid</i>	<i>Powder</i>
T/L and C/L	0.1350	0.3825
T/C and T/T	0.1225	
LTL (drums)	0.1425	0.3875

Reviews on the reactions and uses of sodium methylate have been published by Sittig (80) and by Byrkit and Soule (76); Byrkit and Soule have also described the application of sodium methylate in perfumery (81). The major use of sodium methylate is as a reagent in organic chemistry. It may be used either in alcoholic solution or directly in reactions where excess alcohol is undesirable.

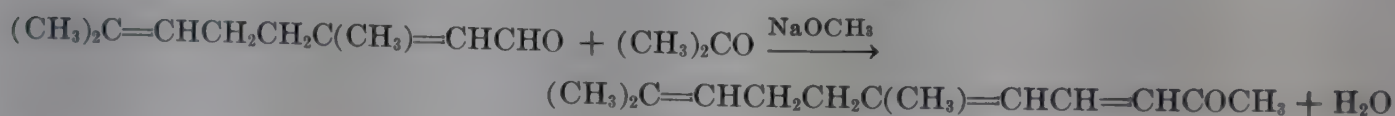
Sodium methylate is an effective catalyst in condensation reactions. There are a large number of these involving aldehydes, ketones, and esters and most of them are well known; consequently, only a few examples will be cited and these are of industrial rather than of laboratory importance.

The condensation of acetate esters with acetone to give acetylacetone is catalyzed by sodium methylate:



The product may be separated from the reaction mixture in the form of its copper salt which is said to have antiknock properties.

The manufacture of pseudoionone for perfumery is carried out by the condensation of citral with acetone in the presence of sodium methylate:



β -Ionone may be prepared in like manner from β -cyclocitral and acetone.

In the manufacture of sulfadiazine, the initial step is the reaction of methyl formate with methyl acetate in the presence of sodium methylate.

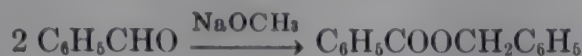


This sodium derivative is then condensed with guanidine to give isocytosine, which is then treated with phosphorus oxychloride, reduced, and condensed with aminobenzene-sulfonyl chloride to yield sulfadiazine.

Barbituric acid may be prepared from malonic ester and urea with sodium methylate.

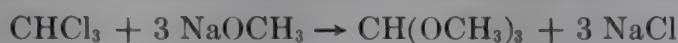


Another reaction which has use in the perfume industry is the self-condensation of aromatic aldehydes to give the aromatic esters in one step (Tishchenko reaction); for example, benzaldehyde to benzyl benzoate:

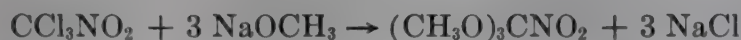


In general, alcohol-free sodium methylate is to be preferred for most condensations (77); sodium methylate prepared in situ was ineffective in ester cyclization but alcohol-free sodium methylate was effective (78). Also, in the condensation of various alkyl acetates it has been reported (79) that high yields depend on the use of alkoxides of great purity.

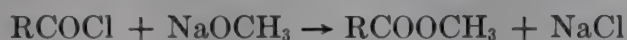
The reaction of sodium methylate with halogen compounds is also important. Organic orthoesters may be prepared from sodium methylate and polyhalogen compounds which contain three chlorine atoms on a terminal carbon atom. The simplest example is the preparation of methyl orthoformate from chloroform:



Higher orthoesters are in commercial use for further synthesis, such as condensation with aromatic amines to form triphenylmethane dyes. Similarly, sodium methylate and chloropicrin give a methyl orthocarbonate which is also used for further synthesis:



Sodium methylate reacts with organic acid chlorides to give methyl esters:

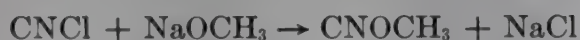


In like manner thiophosphate esters may be prepared from thiophosphoryl chloride and sodium alkoxides, and phosphate esters from phosphoryl chloride.

In the Williamson reaction, sodium methylate and alkyl or aryl halides form ethers:



Cyanogen chloride reacts with sodium methylate to give methyl cyanurate:

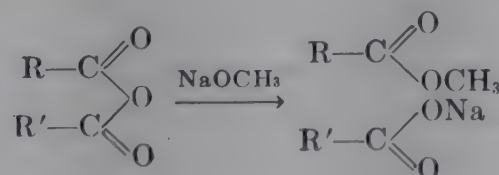


Reaction between metal chlorides and sodium methylate provides a method of wide applicability for the preparation of metal methylates:

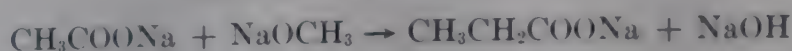
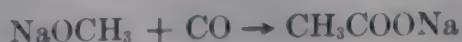


This reaction, which is described more fully under Preparation, is used in the recovery process for polyolefins; the sodium methylate neutralizes the metal chloride catalyst.

In the neutralization of organic and inorganic acids with sodium methylate, methyl alcohol is liberated rather than water, and is much more easily removed to yield anhydrous salts. Fatty acids thus neutralized produce soaps in anhydrous condition; sodium sulfide or hydrosulfide may be produced in a high state of purity by the complete or partial neutralization of hydrogen sulfide with sodium methylate. Anhydrides of polybasic organic acids react with sodium methylate to give a salt and an ester.



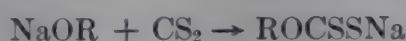
Other reactions of commercial importance are as follows: Sodium methylate enters into addition reaction with carbon monoxide under pressure to give products with longer carbon chains.



Sodium cyanate, which is useful in organic synthesis for the preparation of ureas and semicarbazides, may be prepared from urea and sodium methylate:



Xanthate flotation reagents for use with ores may be manufactured by the reaction of sodium alkoxides with carbon disulfide.



This is but a brief survey of the many reactions in which sodium methylate is used as a reagent in the formation of commercially important compounds. Greater detail may be found in the two reviews by Bradley (39,40).

Tetraisopropyl Titanate (titanium tetraisopropoxide), $\text{Ti}(\text{OPr}^i)_4$, is a white- to light-amber-colored liquid which fumes in moist air; formula weight 284.22, melting point 20°C , boiling point 232°C , density 0.9951. Titanium alkoxides have been known since 1869, but it is only very recently that any industrial demand for them has developed. Commercially, tetraisopropyl titanate is manufactured by reacting titanium tetrachloride with isopropyl alcohol in the presence of ammonia, filtering off the ammonium chloride formed, and vacuum distilling the product. This commercial method of manufacture was introduced in 1938 by Nelles of I. G. Farbenindustrie. Again, alcohol interchange with higher alcohols is a very convenient method for preparing the titanate of higher alkoxy radicals. Tetraisopropyl titanate, tetrabutyl titanate, and tetra-2-ethylhexyl titanate are produced commercially in the United States by the Pigments Division of E. I. du Pont de Nemours & Company, Inc., and by the Anderson Chemical Division of Stauffer Chemical Company. It is also manufactured by Peter Spence, Ltd., in England. There are again no U.S. Tariff Commission reports on these materials, but estimates place production at around 400,000 to 500,000 pounds per year. The commercial grade of titanium isopropoxide is presently available up to multiple drum quantities, and is priced from \$0.90 to \$1.25 per pound. Isopropyl titanate and alkyl titanates in general are used as gelling, curing, and drying agents for natural resins, epoxy resins, alkyds, and silicones. Some are used in combination with aluminum powder in the formation of heat-resistant paints and antifouling compositions; others, in combination with silicones, fatty acids, and stearates, produce excellent water repellents. Still other uses are as adhesion promoters for paint and plastic films and as antibleeding agents in inks and dyes. Chemically they are used as catalysts in one process for preparing linear polycarbonates from self-condensing bis-carbonates; as a catalyst for the preparation of phthalocyanines; and, more recently, as components of polymerization catalyst systems for polyolefins.

Antimony Isopropoxide, Magnesium Methoxide, and Vanadyl Butoxide ($\text{Sb}(\text{OPr}^i)_3$, $\text{Mg}(\text{OMe})_2$, $\text{VO}(\text{OBu})_3$), are all produced in semicommercial quantities by Anderson Chemical. Antimony isopropoxide is used in flameproofing formulations; magnesium methoxide, as a dielectric coating and as a drying and thixotropic gelling agent; and vanadyl butoxide, as a component of catalyst systems for polyolefins.

Zirconium Alkoxides, notably isopropyl and butyl zirconate, are being offered by Harshaw Chemical and Anderson Chemical. Their applications are similar to those of alkyl titanates, but they form more stable compounds and complexes than the corresponding titanium alkoxides; they are preferred in many water-repellent and catalyst formulations.

Other metal alkoxides which may have commercial application are those of *niobium* and *tantalum*, since fractional distillation provides a means of separating these two elements. The distillation of uranium pentaethoxide has been patented (82) as a means of enriching the uranium-235 isotope.

Several metal alkoxides are prepared in fairly sizable quantities and used intraplant for captive applications. This is particularly true of those alkoxides which have limited stability and almost of necessity must be prepared and used in situ. Alkoxides and chloroalkoxides of tetravalent vanadium, and alkoxides of trivalent titanium, which are all sensitive to oxidation by air and have application in the catalyst field, are examples. Many of the aluminum alkoxides, such as aluminum isopropoxide in the manufacture of Chloromycetin and the *t*-butoxide in the preparation of drugs for treatment of athlete's foot, are also prepared and used in situ.

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ALKYD RESINS

The term "alkyd" was originally used by Kienle in 1927 to describe the reaction products of polyhydric alcohols and polybasic acids. Extensive commercialization of special classes of polymeric esters which are not recognized as alkyds has forced a more limited definition. For example, among the polymeric esters which are alkyds by Kienle's definition are the unsaturated polyesters polymerized with styrene, the saturated polyesters reacted with isocyanate, and the so-called "super" linear polyesters of terephthalic acid. These polymers are not considered here (see Urethan polymers; Polyesters; Polyester fibers). The term "alkyd" now tends to specify polyester products composed of polyhydric alcohols, polybasic acids, and monobasic fatty acids. These materials are used chiefly in the coatings industry. In this industry the terms alkyd, alkyd resin, and alkyd solution are used interchangeably, even though most alkyds are handled as solutions in hydrocarbon solvents (30 to 70% by weight of alkyd resin).

The term "modified alkyd," which formerly was used to describe these products, now is associated with chemical modifications which are carried out during alkyd preparation, and which incorporate chemical agents of types other than those included in the definition. For example, if rosin (a mixture of diterpene resin acids and non-acidic components) is added as part of the monobasic acid in an alkyd preparation, the alkyd is considered a rosin-modified alkyd. In this article, the use of "modified" will be restricted to this meaning of chemical modification. When no fatty acids are used, or when they are completely replaced by other types of acid, the products can be considered as "oil-free" alkyds. Rosin is used to replace the fatty acids in a wide variety of commercial products (see Rosin and rosin derivatives). Other commercial "oil-free" alkyds include glycerol terephthalates and water-soluble resins such as the glycol esters of 1,3,5-benzenetricarboxylic acid or the glycol-maleate ester of pentaerythritol.

The term "alkyd blend" will be used for the physical mixture formed by "cold-cutting" an alkyd solution (mixing with it another resin or polymer solution at moderate temperatures) (see Raw materials, p. 861). For example, an alkyd solution cold-cut with nitrocellulose will be considered an alkyd-nitrocellulose blend. With certain ingredients physical mixing with the alkyd is carried out at elevated temperatures in the alkyd reaction vessel by the manufacturer. Such mixtures fit the definition of alkyd blend.

In actual fact and practice, even in the coatings industry, these definitions are by no means precise and often are interchanged. Moreover, the historical metamorphosis which has occurred in these definitions can be very disconcerting, inasmuch as the

term alkyd once was applied strictly to the polybasic acid–polyhydric alcohol product and the incorporation of a monobasic fatty acid was considered to give a modified alkyd.

History. The condensation polymerization reaction by which polyhydric alcohols and polybasic acids form polymers with resinous characteristics has long been known. Berzelius (1) in 1847 obtained a brittle, resinous polymer, the first polyester condensation product, from the reaction of tartaric acid with glycerol. The first systematic investigation of polyester resinous products was attempted in 1856 by Van Bemmelen (2), who prepared glycerides of succinic acid, of citric acid, and of a mixture of succinic and benzoic acids. Additional studies on these types of polymers were made by Debus in 1856 (3), Lourenco in 1863 (4), and Furaro and Danesi in 1880 (5). Ethylene glycol esters were prepared in 1859 by Desplatz (6) from *D*-tartaric acid, and in 1894 Vorländer prepared maleate, fumarate, and succinate polyesters of ethylene glycol.

The brittle, glassy glycerol–phthalic anhydride polymer was first prepared by Watson Smith in 1901 (8). The initial stimulus toward detailed research on alkyd resins came from the electrical industry when the General Electric Company in 1912 investigated these polymeric products because of their heat convertibility characteristics. Callahan (9), Friedburg (10), Arsem (11), Dawson (12), and Howell (13) of the General Electric Laboratories studied the glycerol–phthalic anhydride reaction intensively. They pointed out that when part of the phthalic anhydride was replaced by a monobasic acid, such as oleic, the products were more flexible and had better solubility properties than the glycerol phthalates.

The full potentialities of alkyd resins were not realized until the development of glycerol phthalate containing unsaturated fatty acids. Kienle of General Electric generally is credited with making this significant contribution in 1927 (14). Since then the alkyd resins have carved a place in the protective coatings industry. Several important discoveries, made during and shortly after World War I, helped. Among these discoveries were a practical process for the catalytic oxidation of naphthalene to phthalic anhydride, manufacture of many new industrial solvents, and the development of low-viscosity nitrocellulose solutions.

The search for improved alkyd resins has played a major role in the commercial availability of many new chemicals. The importance of color and cost has led to fractionated, high-molecular-weight monobasic acids, such as lauric, soya, and tall-oil fatty acids. Alkyd resins have been largely responsible for the commercial availability of such polybasic acids as fumaric, maleic, and isophthalic, and for polyhydric alcohols such as pentaerythritol, dipentaerythritol, and trimethylolethane (2-(hydroxymethyl)-2-methyl-1,3-propanediol).

With the successful use of alkyd resins as decorative and protective finishes, the entire coatings industry became synthetic-minded, and many kinds of reactive functional materials were used to modify alkyd resins and expand their use. The many variations in properties through compositional change which the alkyd resins afford is another prime reason for their success. By suitable variations, alkyds have been made for blending with a large number of other resins and polymers to provide an almost endless array of improved products for the coatings industry.

For these two reasons—the improvement of alkyds through modification with new chemicals and their versatility in blending with, and improving upon, properties of

other surface-coating materials—alkyd resins should be important factors in this industry for years to come. A complete list of commercial alkyds, trade names, and suppliers is provided by the National Paint, Varnish, and Lacquer Association (15). See also Coatings, industrial; Paint.

Outline of Manufacture. The main chemical reactions involved in alkyd preparations are esterification and ester exchange. A batch process is generally used for manufacture. The exact procedure depends on the types of ingredients used and the properties desired in the alkyd. Alkyd preparations are usually carried out at elevated temperatures (above 200°C) (see Manufacture, p. 868). When the reaction is completed most alkyds are diluted (thinned) at elevated temperatures in another vessel with solvent, chiefly hydrocarbons, to a resin concentration of about 30 to 70% by weight. These solutions are filtered and stored for sale or further processing.

Classification of Alkyd Resins

The alkyds, as finished solutions, are ready for cold blending with other resins or polymer solutions for use in clear finishes; or for use as vehicles in which to grind pigments prior to blending with other resin or polymer solutions; or for grinding with pigments to form finished alkyd paints. More than 90% of the alkyds produced are handled in one of these ways to produce some type of paint, varnish, or lacquer for industrial or home consumption. About half of the alkyds made are sold by their producers to others who carry out the final operations of manufacture of a paint or other coating material. The remainder of the alkyds are converted directly by their manufacturers to finished coatings products. The bulk of these finished coatings are sold as pigmented products.

Because of the wide variety of commercial alkyds, they are further classified by the coatings industry. The following widely used classification is related chiefly to the kind of monobasic fatty acid in the alkyd:

1. *Drying.* The monobasic fatty acid has an unsaturated structure present in sufficient quantity to cause a thin film (1–3 mils) of the alkyd to polymerize in the presence of oxygen at room temperature to give a coherent, solid film.

2. *Nondrying.* The amount of unsaturated structure in the monobasic fatty acid is so low that little or no polymerization occurs with oxygen.

The drying alkyds are often used alone in coating vehicles; nondrying alkyds are blended with other polymeric materials to give finished products. Obviously these classifications are somewhat arbitrary and various degrees of drying can exist. As a matter of nomenclature, alkyds which are intermediate in behavior are sometimes considered semidrying.

The monobasic fatty acid content of an alkyd may be added as such, or it may be added in the form of a triglyceride, which is commonly referred to as an oil. Vegetable oils such as soybean or soya oil are currently the predominant oils used in alkyds. Prior to the commercialization of monobasic fatty acids such as tall-oil fatty acids, soya acid, and lauric and coconut acids, oils were the only source of the monobasic fatty acid component for alkyds.

Alkyds are also classified according to the amount of oil and phthalic anhydride present in the alkyd. The generally recognized compositions are as follows:

<i>Type oil</i>	<i>Oil content, %</i>	<i>Phthalic anhydride, %</i>
short	35-45	>35
medium	46-55	30-35
long	56-70	20-30
very long	71 up	<20

The content of any ingredient in an alkyd may be defined and determined by the following expression:

$$\text{content as wt \% of } x = \frac{\text{weight of } x \text{ charged to alkyd}}{\text{theoretical weight of finished alkyd}} \times 100$$

where x may be phthalic anhydride, oil, monobasic fatty acid, polyhydric alcohol (also called polyol), or other reagent. Since water is lost in the esterification, it is possible for the percentages of the ingredients to add up to more than 100. Use of the oil content classification and the drying or nondrying concept leads to alkyd descriptions such as a 60% oil-drying alkyd, or, with less precision, a long-oil-drying alkyd.

When monobasic fatty acid is used instead of an oil, yet another type of nomenclature is required. For example, an alkyd prepared from tall-oil acid, pentaerythritol, and isophthalic acid might better be described by percent fatty acid content. This classification is enjoying a greater degree of popularity, especially as inexpensive tall-oil fatty acids have been used in alkyds in increasing amounts in recent years. For example, federal government specifications for alkyds define alkyd composition by this method. However, if the alkyd contains 60% fatty acid and is called a 60% fatty acid alkyd, the description is still not complete. To avoid this problem the alkyd is referred to specifically as a 60% fatty acid pentaerythritol-isophthalate alkyd. Comparisons between the long-oil, short-oil system and the percent fatty acid system can be made by stoichiometrically converting the weight of fatty acid to the weight of an equivalent molar amount of triglyceride.

The most serious deficiency in the classification system arises if monobasic acids of widely differing molecular weights are used. For example, from the same molar ratios of pentaerythritol and phthalic anhydride and monobasic fatty acid, both a 60% tall-oil fatty acid alkyd and a 45% pelargonic acid alkyd would be possible. The latter, however, would be termed a short-oil, nondrying alkyd, and the former a long-oil-drying alkyd. A classification scheme based on molar ratios has been proposed by Kraft (16).

For our purposes here, however, the classifications described will be used regardless of their limitations.

Chemical Reactions

The chemical reactions that occur during preparation of alkyd resins are as follows:

1. Condensation reactions among alkyd ingredients or alkyd modifiers, including esterification; ester, alcohol, or acid exchanges; and etherification.
2. Addition reactions of the unsaturated hydrocarbon portions of the monobasic fatty acids, including free-radical or Diels-Alder reactions with other alkyd ingredients, modifiers, or oxygen.

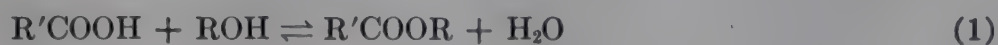
3. Addition reactions, especially free-radical types, with other unsaturated alkyd ingredients.

4. Side reactions such as decarboxylation.

Chemical reactions during use or formation of a film include polymerization reactions during air-drying of alkyds, and reactions in alkyd blends, especially during heating.

Because of the complex composition of alkyds, an understanding of the chemistry of their behavior in the kinds of reactions cited is best derived by inference from the chemistry of simpler systems. For this reason and because of the scope of chemistry involved, only broad generalizations and examples are presented here. References are made to more detailed studies.

Esterification and Ester Exchange. The basic reaction involved in the preparation of all alkyd resins is esterification (qv), one of the most familiar of organic chemical reactions. As an equilibrium system the reaction is reversible as shown in equation 1.



The general principles of esterification apply to alkyd resins, but some of the following specific considerations are especially pertinent to alkyd resin preparation. The technique of using a molar excess of one reactant to help effect complete reaction must be viewed in terms of the practical difficulty of removing any excess ingredient from an alkyd resin. Any excess of a constituent either becomes part of the alkyd structure or remains as a physical mixture, and in any case affects the properties.

Both the polyhydric alcohols and the polybasic acids used obviously have more than one reactive group per molecule. The statistical probabilities for complex mixtures of products therefore increase exponentially. If a stoichiometric amount of pentaerythritol is used in place of a monohydric alcohol in equation 1, the resultant ester mix could contain mono-, di-, tri-, and tetraester at equilibrium, as well as unchanged pentaerythritol. If, in addition, the monobasic fatty acid is composed of many isomers, as is tall-oil fatty acid, the resulting mixture of products could be of extreme complexity. The inclusion of a polybasic acid such as phthalic anhydride even further compounds the possibilities.

Ester exchange or transesterification is illustrated in equation 2.

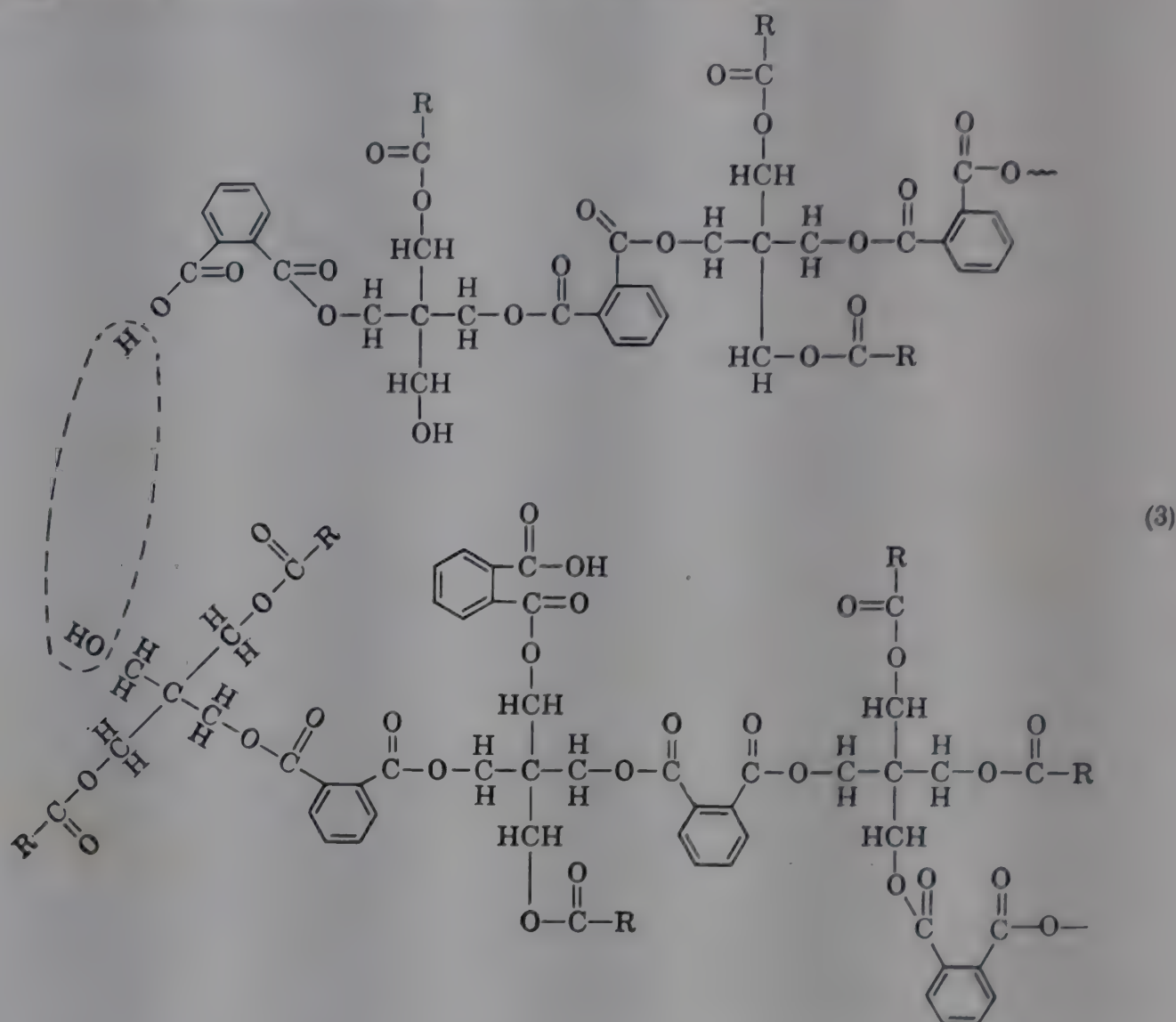


Because this reaction can occur between any two ester molecules, it is of importance in alkyd preparations, especially for its effect on the molecular-weight distribution in the final product.

Linear polymers result if both the acid and alcohol have only two reactive (functional) groups each. However, as any one ingredient with more than two reactive groups is introduced, so is the possibility introduced of chain-branching in molecules and crosslinking among various molecules.

Many of the ultimate coating applications of alkyds have the implicit requirement that the alkyd be capable of gelation. However, such gelation is desired only after the paint or other coating vehicle has been applied to the substrate. Crosslinking to the point of gelation (indicated by insolubility and infusibility) before application is undesirable because such insoluble, infusible resins are intractable.

Some possibilities for branching and crosslinking when the functionality of one of the reagents is greater than two are shown in equation 3 (R = monobasic fatty acid), where the effect of tetrafunctional pentaerythritol is illustrated. Although only two alkydlike molecules are indicated and the dotted area represents only one possible crosslinking reaction site, any and all reaction sites (including ester groups) in these or other molecules can be considered in the actual alkyd reaction. As the interconnecting network becomes infinite, gelation or infusibility results.



Attempts to rationalize the observations of crosslinking behavior in terms of esterification reactions, alkyd structure, and functional-group concepts were initiated by Kienle (17-19). Carothers (20) derived mathematical equations to forecast the extent of esterification reaction necessary to produce gelation in systems containing ingredients with more than two functional groups. The equations were based on mass-action laws and on the assumption that the molecular weight at the gel point is infinite.

The Carothers equation, when applied to bifunctional compounds, indicates no gelation, even though 100% esterification occurs. When this equation is used to calculate the degree of esterification necessary to cause the gelation of a stoichiometrically equivalent mixture of pentaerythritol and adipic acid, the result is 75%. However, the experimental value observed by Flory (21) for this system is 60%.

Flory (22) introduced the application of probability statistics to the prediction of gelation as a logical refinement to explain the wide discrepancy obtained above. By

use of a branching index his prediction for this system would be 57%. The branching index took into more precise account the statistical requirement that in any system where bifunctional molecules are also present, gelation occurs only when chains include more highly functional, unterminated ingredients.

Flory also recognized in his approach that all molecules were not of infinite size at gelation. Actually only a relatively small proportion were of infinite size. (By a molecule of "infinite" size is meant one so large that no appreciable change in properties would result from a further increase in its size.) Stockmayer (23) provided more general equations, but also used the original Flory assumptions of equivalent reactivity of similar functional groups and absence of intramolecular reactions. Jonason (24) has applied Flory's treatment (21,22) to alkyds specifically to assess the effect of Flory's assumption of equal reactivity of identical functional groups (eg, all —COOH). The results indicate that for practical purposes, differences in reactivity among primary hydroxyl ($\text{—CH}_2\text{OH}$) and secondary hydroxyl (>CHOH) groups in a number of polyols do not influence the degree of esterification at gelation. However, Jonason found that modified equations were necessary because of considerable differences in the reactivity among the carboxyl groups of aliphatic and aromatic acids. In spite of these corrections, percentage discrepancies between observed and calculated extent of reaction, P , ranged from 3 to 9%. Because P (observed) was almost always greater than P (calculated), Jonason (24) attributes the discrepancies to intramolecular condensation, which would have this effect.

Wiederhorn (25) and more especially Patton (26), in a book devoted to the subject, have applied some aspects of these mathematical concepts to the formulation of alkyd resins. These mathematical concepts are not yet sufficiently rigorous to apply without experimentally derived correction factors. Complications in extending the theory with sufficient accuracy to a practical alkyd recipe without experimental verification arise from a number of factors. These include the aforementioned lack of uniform reactivity of all groups of equal functionality, intramolecular reactions, esterification, and polymerization of unsaturated acids. Each of these factors affects the effective functional-group content of the polymeric mixture.

However, the theories are sufficiently precise to fortify the concept that most alkyds should be formulated so that the degree of esterification ranges from 90 to 100% without gelation. The alkyd formulator satisfies this requirement in the pentaerythritol-adipic acid system (gelation point = 60% esterification), for example, by incorporating a monofunctional reagent into the reaction mixture. Although monofunctional alcohols, such as hydroabietyl alcohol, provide an approach, the most widely used method has been the addition of a monobasic fatty acid. Stoichiometric changes in the original polyhydric alcohol-polybasic acid composition are also necessary to give a composition having low acidity at the high percentage of esterification. In alkyds that are medium or short by fatty acid content, excesses of polyhydric alcohols generally are used to permit essentially complete esterification of the acid groups. This general approach is taken because residual acidity is more detrimental to alkyd and coating properties than residual hydroxyl content.

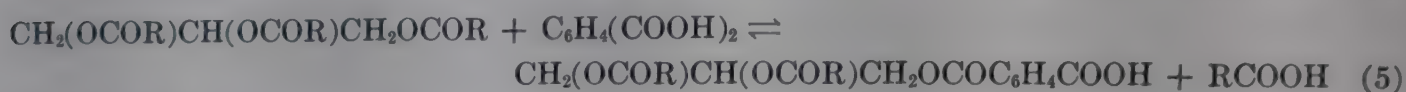
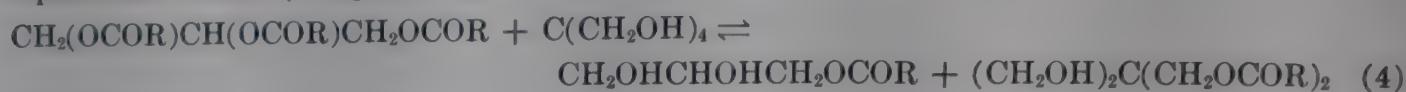
Monobasic fatty acids are the chief approach to the reduction of functionality because they provide solubility, flexibility, and drying, or other desirable properties to the alkyd resin.

Alkyd modifiers that can react with hydroxyl, carboxyl, or ester groups likewise enter the alkyd structure through addition or condensation reactions. Examples are

isocyanates, epoxides, amines, phenolic resins, formaldehyde, and polyamides; acid modifiers such as rosin and benzoic acids; and hydroxyl-containing modifiers such as hydroabietyl alcohol and silicones.

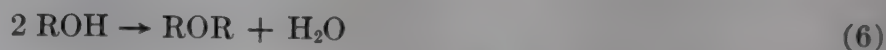
Alcoholysis and Acidolysis. These reactions are actually special cases of esterification in the sense that only hydroxyl, carboxyl, and ester groups are involved.

A partial alcoholysis and a partial acidolysis of a triglyceride are illustrated by equations 4 and 5, respectively.

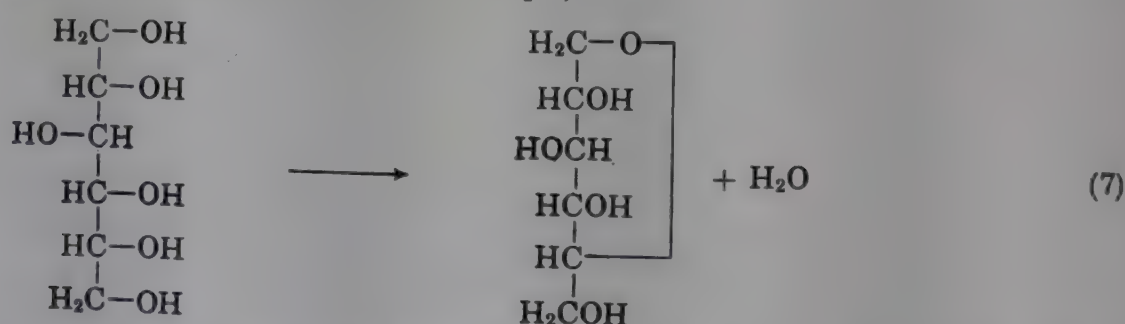


Both alcoholysis and acidolysis are reactions used in the preparation of alkyds from oils. If, for example, a polyol and phthalic anhydride are added to the oil simultaneously, substantial amounts of insoluble polyol phthalate form. To avoid this difficulty, either alcoholysis or acidolysis is employed to make partial esters of the polyol or acid, respectively, before proceeding. The acidolysis reaction is, however, less extensively used. The alcoholysis reaction in alkyd preparation is discussed in greater detail on p. 868.

Etherification. At the temperatures of alkyd processing (typically 210–250°C), reactions other than esterification can occur with relative ease. Etherification of the polyols may occur.



At 280°C Brett (27) found as much as 27% etherification with glycerol as the polyol but he found this amount only during alcoholysis when an excess of glycerol and an alkaline catalyst were present. At a more conventional temperature, 240°C, he found less etherification—8% with glycerol. He reported little etherification with pentaerythritol at 240°C. Sorbitol is more prone to etherification than glycerol because it is capable of internal etherification (eq 7).



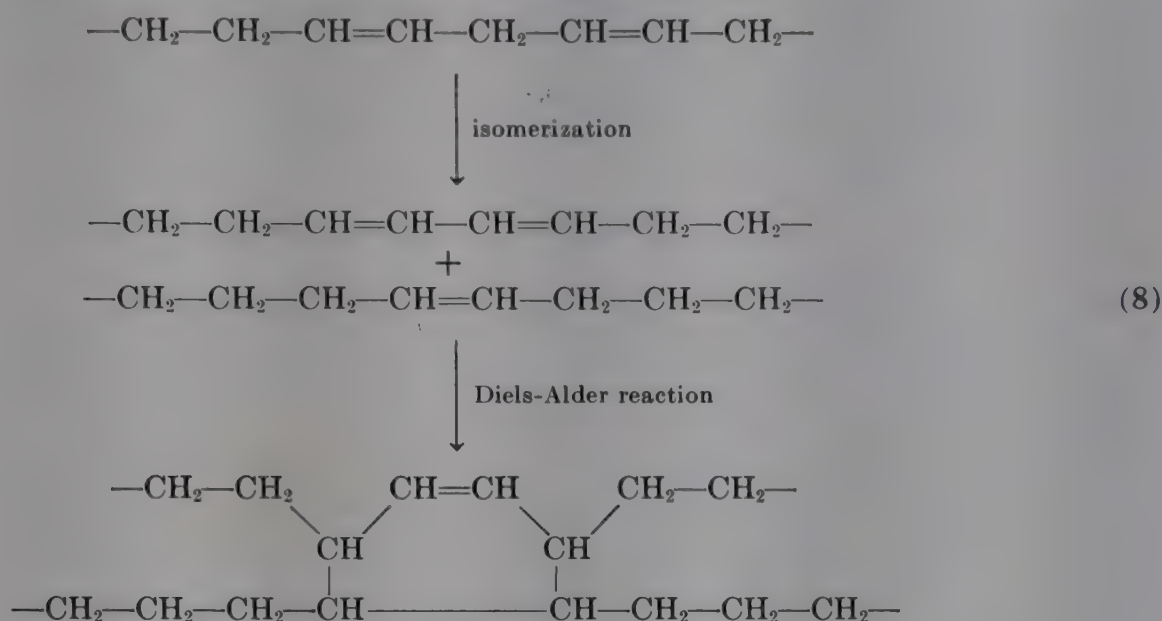
Addition Reactions of Unsaturated Monobasic Fatty Acids. The noncarboxylic reactions of monobasic fatty acids that are pertinent to alkyd chemistry are dependent upon unsaturation in the acid. Reactions in which there are single double bonds and conjugated pairs of double bonds can occur by both free-radical or Diels-Alder mechanisms. The manner in which the reaction proceeds depends on the reagent, but may be related to the type of unsaturation in the fatty acid. Reactions with oxygen, for example, are free-radical reactions regardless of the type of acid. During preparation, reaction of alkyds with oxygen is generally an undesirable side reaction. Because the extensive polymerization which can be initiated by oxygen is not required, alkyds, in contrast to oils, are rarely “blown” (sparged by air).

Vinyl-type modifiers, such as styrene, vinyltoluene isomers, methyl and other esters of methacrylic acid, and acrylonitrile can react by free-radical addition. With

styrene, free-radical reactions are most likely to occur when nonconjugated fatty acids are used. Conjugated fatty acids apparently react with styrene by a Diels-Alder route (28). Some free polystyrene may also be present. Styrenated alkyds are the most important of those modified with vinyl monomers.

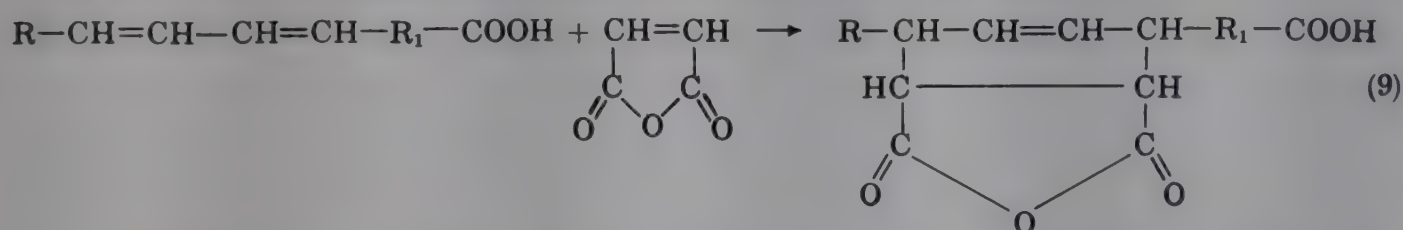
Other important Diels-Alder reactions in alkyd preparations include the thermal polymerization of unsaturated fatty acids, maleic anhydride addition, and possibly phenol-formaldehyde resin addition.

Thermal polymerization involves at least one conjugated fatty acid, which may be formed by isomerization of double bonds.

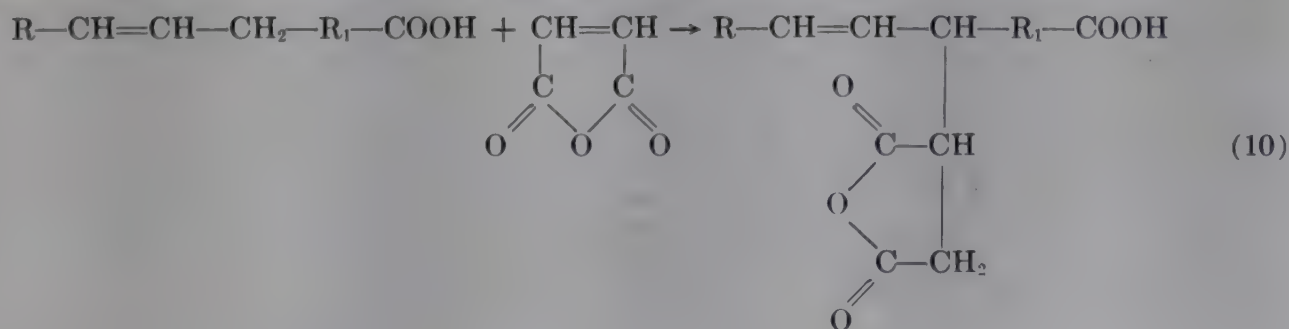


This reaction is sometimes referred to as "heat bodying" because higher viscosities result. Oils such as tung and oiticica "body" readily and consequently are little used as the sole acid source in alkyds. Linseed oil is more moderate in bodying rate except at elevated temperatures. In solvent-processed, 70% linseed oil alkyds, Brett (27) has reported a 25% thermal polymerization of fatty acid after 7 hours at 280°C, but only 6% after 30 hours at 240°C. Soya oil or tall-oil fatty acids show little thermal polymerization at 240°C.

Maleic anhydride undergoes Diels-Alder reactions with unsaturated fatty acids. Fatty acids with conjugated unsaturation react as shown in equation 9.

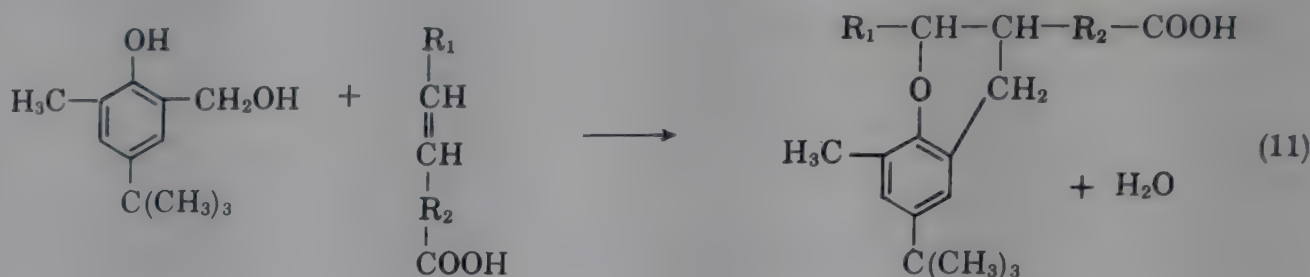


With fatty acids containing only one double bond, a Diels-Alder reaction of a different type can occur (often referred to as a Diels-Alder reaction of the second type).



These reactions with maleic anhydride or fumaric acid are widely used by alkyd chemists to increase the viscosity of alkyds and give them better color and ultimate coating hardness.

Cyclopentadiene is another important ingredient for alkyds which adds to unsaturated fatty acids by the Diels-Alder mechanism. Other important examples of unsaturated fatty acid reactions are those with phenol-formaldehyde condensates. Chroman-type structures have been reported (29) as indicated in equation 11.



Some authorities (30) consider that the chroman products arise through a Diels-Alder reaction mechanism. However, the chemistry of phenol-formaldehyde reactions is extremely complex and other reactions, including ionic condensation reactions, can also occur.

Addition Reactions With Other Unsaturated Alkyd Ingredients. Unsaturated alkyd ingredients, other than monobasic fatty acids, also serve as points for modification by both Diels-Alder and free-radical addition reactions. Frequently unsaturated dibasic acids, such as maleic or fumaric, provide the reactive unsaturation for either free-radical addition of vinyl-type monomers or reaction with dienes such as rosin. Phthalic anhydride may or may not be an additional ingredient in these systems (see Raw materials, p. 861).

Reactions During Coating Formation With Drying Alkyds. Polymerization of drying alkyds is initiated by autoxidation. These reactions have been widely investigated with drying oils (qv) (31). Medium- and long-oil alkyds, because of their molecular structure, provide more reaction sites than a drying oil containing the same fatty acid composition, and, therefore, react more rapidly than the oil.

Reactions During Coating Formation in Alkyd Blends. The study of these reactions is restricted because the products usually become infusible, intractable masses. Relatively little is known about this subject. If drying alkyds are used in the blend, the usual polymerization initiated by air can be accompanied by reactions such as those considered above, or reactions of the blending agent with itself. With nondrying alkyds, which are essentially plasticizers, only further condensation reactions through hydroxyl, carboxyl, and ester groups are likely.

Molecular Structure. An alkyd resin can be considered as a hard resin (the glycerol phthalate or other polyol-polybasic acid condensate) plasticized by fatty acid, all in one molecule. In a sense, then, an alkyd represents an improvement over a drying oil or a varnish, which is chiefly a physical mixture of hard resin dissolved in a drying oil (plasticizer).

Adjustments can be made in the polyol-polybasic acid chain by selection of the polyol or polybasic acid to give degrees of hardness, flexibility, toughness, and chemical resistance. By variation of the amount and kind of fatty acid substituent, solubility, subsequent reactivity, and viscosity can be modified.

The number average molecular weight of alkyds generally ranges from approximately 2000 to 3000; there is generally, however, a very broad spectrum of molecular-weight distribution (27).

Raw Materials

The most common alkyd ingredients are as follows:

Polybasic acids		Oils	
phthalic anhydride	azelaic acid	linseed	safflower
isophthalic acid	succinic acid	soya	oiticica
maleic anhydride	adipic acid	dehydrated castor	cottonseed
fumaric acid	sebacic acid	tung	coconut
		fish	
Polyhydric alcohols			
glycerol		trimethylolpropane (2-ethyl-2-	
pentaerythritol		(hydroxymethyl)-1,3-propanediol)	
dipentaerythritol		ethylene glycol	
trimethylolethane (2-(hydroxy-		propylene glycol	
methyl)-2-methyl-1,3-propanediol)		neopentylene glycol (2,2-dimethyl-	
sorbitol		1,3-propanediol)	
		dipropylene glycol	
Monobasic acids			
fatty acids and fractionated fatty acids obtained from oils			
tall-oil fatty acids			
synthetic saturated fatty acids			
pelargonic			
isodecanoic			
isoöctanoic			
2-ethylhexanoic			

Polyhydric Alcohols. The two predominant polyhydric alcohols used in alkyd resins are pentaerythritol (see Alcohols, polyhydric) and glycerol (qv). The high functionality of pentaerythritol makes it of wide interest as the polyol for long-oil alkyds containing 60% or more fatty acid. Because of its high functionality, pentaerythritol is often blended with either glycerol or glycols in alkyds containing less than 60% fatty acids.

Pentaerythritol-containing alkyds tend to have higher viscosities and molecular weights, dry more rapidly, and give coatings of greater hardness with lower flexibility, better gloss and gloss retention, better heat and yellowing resistance, better chemical resistance, better water resistance, and better exterior durability than glycerol alkyds of comparable oil content. In paints, pentaerythritol types also show greater anti-sagging at equal brushability and flow. Pentaerythritol is used especially with slower drying fatty acids such as tall-oil and cottonseed oil fatty acids because alkyds with good drying rates result. The higher functionality of pentaerythritol (four hydroxyl groups) over glycerol (three hydroxyl groups) is the chief reason for many of these advantages.

Many other polyhydric alcohols have been recommended for use in oil-modified alkyds, but the amounts used commercially are very small in comparison with the quantities of glycerol and pentaerythritol used. Sorbitol, a hexahydric alcohol, undergoes intramolecular dehydration (see eq 7) at alkyd esterification temperatures of 210–260°C and is rarely used except in small amounts with pentaerythritol. Other polyhydric alcohols, such as dipentaerythritol, tripentaerythritol, trimethylolpropane, and trimethylolethane, are used in more limited amounts to impart special properties to alkyd resins (see Alcohols, polyhydric).

On the basis of functionality alone, an equimolar mixture of pentaerythritol and ethylene glycol (average three hydroxyl groups) is equivalent to glycerol. However, because of the distribution of molecular weight, branching, and other considerations, the two alkyd compositions cannot be identical. In short- and medium-oil alkyds, use of pentaerythritol–glycol mixtures is increasing because coatings of better water resistance, gloss retention, and durability in comparison with analogous glycerol alkyds result. Higher glycols with greater distance between the hydroxyl groups lead to alkyds with flexibility, solubility, and better compatibility with film formers.

Polybasic Acids. Phthalic anhydride (see Phthalic acids) is by far the most important polybasic acid used in alkyd resins because of its low cost and the excellent properties it imparts to alkyd resin polymers. In recent years isophthalic acid (the meta isomer of phthalic acid) has become more extensively used to supplement and in some cases supplant orthophthalic anhydride alkyds. Isophthalic acid alkyds, in comparison with analogous orthophthalic alkyds, are claimed to have higher molecular weights and higher viscosities; to have better drying characteristics; and to give harder and more durable films with better heat and chemical stability. To produce a long-oil isophthalic alkyd with the same viscosity at a given solids concentration as that of a phthalic anhydride alkyd, the isophthalic alkyd must contain 5 to 10% greater oil content. Isophthalic alkyds also gel more rapidly than comparable orthophthalic alkyds. Both acids have equivalent functionality, but intramolecular cyclization has been postulated as the reason for this behavior (24). Brown (32) has attributed the result to the etherification of the polyol in the presence of isophthalic acid.

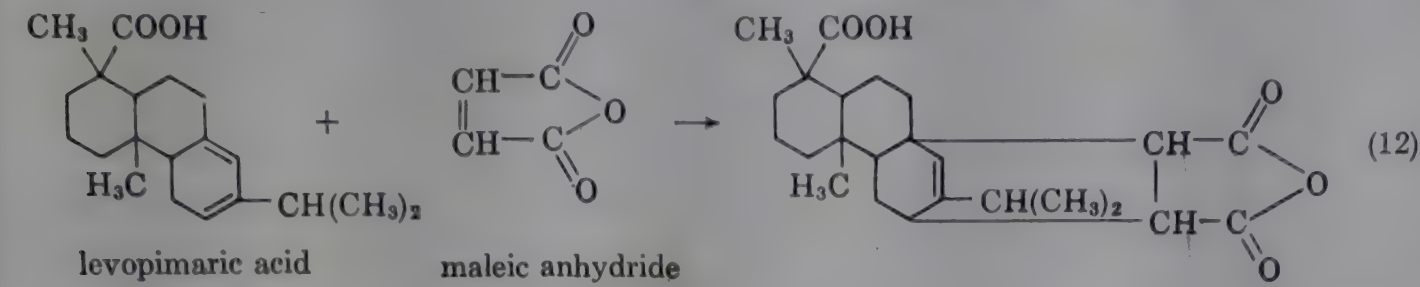
The para isomer of phthalic acid, terephthalic acid, has very poor solubility in alkyd ingredients. This, coupled with its very high melting point (436°C), has made the processing of terephthalic-based alkyds very difficult. Its dimethyl ester, being both soluble and low melting, can be processed readily but only unusual applications justify its higher cost.

Other dibasic acids used in alkyds in limited amounts include tetrahydrophthalic anhydride (*cis*-4-cyclohexene-1,2-dicarboxylic anhydride), hexahydrophthalic anhydride (*cis*-1,2-cyclohexanedicarboxylic anhydride), tetrachlorophthalic anhydride (3,4,5,6-tetrachloro-1,2-benzenedicarboxylic anhydride), maleic anhydride, fumaric acid, and dimerized fatty acids (see Fatty acids).

Maleic and fumaric acids (see Maleic acid) often are used to replace part (up to about 10% on a molar basis) of the phthalic anhydride in the alkyd resin. Because they react with the unsaturation in fatty acids (see eq 10), their effect is to increase the total functionality of the alkyd system. Viscosities and polymer molecular weights otherwise not attainable from any given fatty acid–polyhydric alcohol–phthalic anhydride combination result. When maleic and fumaric acids are used in small amounts in phthalic anhydride alkyds, they dry more rapidly and give harder films

with improved color, better alkali resistance, and better exterior durability because of improved water resistance and adhesion.

Maleic and fumaric acid often are combined with rosin (qv) by the Diels-Alder reaction. Tribasic adducts such as the one shown in equation 12 are formed.



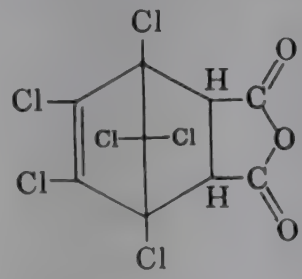
Alkyds with either rosin–maleic acid, maleic anhydride, or fumaric acid adducts as the polybasic acid are used in many low-cost coating applications, but the films from these resins do not have the color retention, toughness, adhesion, gloss retention, or exterior durability that the phthalic anhydride alkyds have.

The glycerol esters of phthalic anhydride and maleic anhydride are hard, brittle resins, but the corresponding esters of succinic, adipic, azelaic, and sebacic acid are softer owing to structural differences. These linear dibasic acids often are used in plasticizing or nondrying alkyds which are blended with various film formers.

There are several other maleic anhydride adducts that are used to a limited extent in several types of alkyd coatings. Petrex (trademark of Hercules Powder Company) is made by addition of maleic anhydride to unsaturated terpenes. Structures present include the following:



Chlorendic anhydride (trademark HET, Hooker Chemical Company) is made from hexachlorocyclopentadiene and maleic anhydride.



Fatty Acids and Oils. (See Fats and fatty oils; Fatty acids.) The extent and kind of unsaturation in the drying fatty acids has a strong bearing on the properties of the finished alkyd. In general, triene unsaturation contributes more to drying rate, color properties, and film hardness than diene unsaturation. Conjugated systems are slightly better than nonconjugated systems in the development of initial drying. The monounsaturated and saturated portions have little drying tendency. Saturated acids appear to inhibit drying performance. The effect of oil type on alkyd properties which, of course, will carry through to the pigmented finishes, is shown in Table 1.

Table 1. Effect of Type of Oil on Alkyd Properties

Triglyceride or fatty acid source	Iodine value ^a	Speed of dry	Coating properties ^b	
			Color retention	Gloss ^c retention
tung	170	↑	↓	↑
linseed	180			
dehydrated castor	155			
safflower	140			
segregated cottonseed	130–			
	140			
tall-oil fatty acid	125			
soya	135			
cottonseed ^d	110			
peanut ^d	108			
castor ^d	85			
olive ^d	85			
coconut ^d	9			

^a Grams of iodine absorbed/100 grams of oil or acid.

^b Properties increase or improve in arrow direction.

^c The gloss-retention arrow is reversed when the alkyd is blended with urea and melamine resins and used in baking enamels. For example, a coconut alkyd-amino resin blend will be better in gloss retention than a soya alkyd-amino resin blend.

^d Alkyd blends are required to get useful coatings.

If an oil or acid has an iodine value of 125–135 or more, indicating about 1.5 double bonds per fatty acid, it will confer satisfactory drying properties on the alkyd. Below these iodine values, the oils either do not dry, or take an extremely long time to form a dry film. Tung and dehydrated castor oils give the best drying speeds because in these oils, fatty acid groups of multiple unsaturation predominate over others. Likewise, safflower would be better than segregated cottonseed which, in turn, is slightly better than soybean. The oils and fatty acids with the higher iodine values not only show faster drying properties but also give coatings of greater hardness and better gloss. Iodine values of tall-oil fatty acids, however, require special interpretation because of the presence of iodine-absorbing resin acids which do not enter into the ordinary film-drying reactions.

For products of moderate drying rates and good color retention, the standard alkyds in the United States have been based for many years on low-cost soybean oil. Recently the advent of still lower cost fatty acids derived from tall oil, which give slightly better color retention and satisfactory drying, has resulted in a large increase in their use. For most rapid-drying, but less stringent color-retention requirements, linseed oil alkyds are standard. Dehydrated castor oil is used for color-retentive baking alkyds; soybean oil alkyds are also used for this purpose but are not as beneficial for color retention or hardness. China wood oil by itself undergoes gelation easily so it is generally used in admixture with other oils to produce alkyds which dry rapidly and give films of high hardness and chemical resistance.

In replacing one drying fatty acid in any given alkyd resin with another, it may be taken into account that there is not as much difference among the drying rates of the alkyds as there is in the oils themselves. For example, a soybean-pentaerythritol-phthalate alkyd with 65% oil and 24% phthalic anhydride content, and also its linseed

analog, will both dry in 6–10 hours. On the other hand, linseed oil requires approximately 16–24 hours to reach a dry state while soybean oil takes more than 48 hours.

Nondrying or nonoxidizing alkyds are usually based on coconut or castor oil or short-chain fatty acids and have high phthalic anhydride contents. They will not polymerize by exposure to oxygen but may polymerize further by themselves or interact with other materials (blending agents) upon further heating. Such alkyds are often used in blends with amino resins, nitrocellulose, or chlorinated rubber, where the alkyd contributes plasticity and adhesion. With reactive chemicals such as the amino resins, the finishes are baked to induce polymerization. The coatings have good color retention, flexibility, and durability.

Alkyd resins with 30–48% oil content are diluted with aromatic hydrocarbons such as xylene because of poor solubility in mineral spirits; alkyds with an oil content greater than 48% are usually thinned in aliphatic hydrocarbons such as mineral spirits. According to Earhart (33), the general qualitative effect of the oil content of these alkyd-resin solutions on alkyd, paint, and coating properties is as follows:

1. As the oil content increases, there is an improvement in paint flow and in can stability characteristics, and in ease of brushing and pigment grinding, but there is increased paint sagging.

2. With decreasing oil content, there is an increase in solution viscosity and coating hardness, in initial gloss, and in gloss and color retention, and the initial color is improved.

3. At the 50% oil-content level, properties of rapid drying, water resistance, and exterior durability are at their optimum level.

Driers. (See Driers and metallic soaps) The drying of alkyds is accelerated, much like the drying of triglycerides, by the addition of oil-soluble (organic acid) salts of multivalent metals such as cobalt, lead, and manganese (34). The mechanism of drier action of oxygen-induced polymerization of oil or alkyds is not precisely understood, but the most reasonable explanation is that the metallic portion serves to decompose hydroperoxides to free radicals which initiate polymerization. The organic portion of the salt serves merely to solubilize the metal in the alkyd. Selection of the kind and type of drier is important to optimum speed and uniformity of drying. This selection is influenced not only by the type of oil, oil content, and pigmentation of the alkyd, but by the conditions, such as baking, under which drying occurs. Drier levels or concentrations are usually specified in terms of a weight percentage of metal to resin solids. Generally two metals are used, one for surface drying and the other for drying throughout the coating; the important aspect is to prevent sealing of the coating surface before sufficient oxygen has been absorbed. Drier concentrations often fall in the following ranges: 0.1 to 0.6% lead together with 0.02 to 0.06% cobalt.

Modifiers. On p. 851, alkyd modification was defined as a chemical reaction during alkyd preparation which incorporates into the alkyd chemical agents which do not fit the classification of alkyd ingredients—namely, polyhydric alcohol, polybasic acid, or fatty acid. Although several of the modifiers given in Table 2 might actually be considered as alkyd ingredients, they have been included as modifiers to recognize historical convention rather than precision. The primary reasons for modification are either for economy or to confer some desirable property. A summary of generally recognized advantages and disadvantages of the alkyd and of the resultant coating is given. The amount of modifier may be as high as 40% of the total alkyd, but 10–25% is more common.

Table 2. Effects of Modifiers

Modifier	Advantages	Disadvantages
rosin or rosin ester	faster dry better brushing greater hardness better mar resistance better adhesion	more yellowing decreased exterior durability when used in excess
phenolic	greater hardness better water resistance better alkali resistance better solvent resistance	more yellowing poorer stability drier problems
styrene, vinyltoluene, methyl methacrylate, acrylonitrile	faster dry improved color and gloss improved color and gloss retention improved chemical resistance	poorer solvent resistance
silicones	improved heat resistance greater hardness more resistance to thermal shock	higher cost higher curing temperature
hydroabietyl alcohol (Abitol, trademark Hercules Powder Co.)	better brushing reduces alkyd function- ality and acts as gelation inhibitor better solubility (in aliphatic solvent) better gloss better flow greater hardness	slightly more yellowing slightly decreased durability when used in excess
<i>p</i> -tert-butylbenzoic acid, benzoic acid	reduces alkyd func- tionality and acts as a gelation inhibitor greater hardness higher viscosity faster dry improved color and gloss improved chemical resistance	poorer solubility poorer flexibility
epoxides	improved adhesion better alkali resistance better detergent resistance better solvent resistance	poorer color retention rapid chalking
isocyanates	better water resistance faster dry better abrasion resistance	greater yellowing toxicity problem (in manufacture)

Blending Agents. The components of any alkyd resin and the proportion of these components are varied to suit the intended use of the alkyd. One of the most important properties of alkyd resins is their ability to combine with a large number of other polymeric resins to yield improved products. This fact has vastly extended the use of alkyd resins, and any new polymer or film-forming material is checked for compatibility with various types of alkyd resins. The alkyd resin contributes to the coating flexibility, adhesion, durability, and gloss, and the addition of a polymeric additive may give better hardness, faster drying speed, toughness, corrosion and chemical resistance, heat resistance, and improved color retention.

A wide range of performance characteristics can be achieved by blending. Often the alkyd constitutes the major part of the final mixture, but alkyds are also added in minor amounts when the properties of the main material are emphasized. A good example is the addition of alkyds to synthetic latexes such as styrene-butadiene and polyvinyl acetate to improve the adhesion and water resistance of latex paints made from these emulsion polymers.

Blending is used when the additive material will not withstand alkyd preparation temperatures (over 200°C) or when a severe limitation is placed on the amount which can be added because of reactivity during the preparation. Manufacturers of finished coatings who purchase alkyds often use cold blending to provide the special properties required in their finished products.

Three of the most widely used agents for blending are nitrocellulose, amino resins, and chlorinated rubber. The coating properties of alkyds in which these blending agents were used are compared to those of unblended alkyds in Table 3.

Table 3. Coating Properties of Blended Alkyds

Blending agent	Advantages	Disadvantages
nitrocellulose (see Cellulose derivatives)	faster dry better chemical resistance better solvent resistance greater hardness	poorer durability poorer flexibility lower solids
urea and melamine resins (see Aminoplasts)	better chemical resistance better color and color retention greater hardness faster cure higher heat resistance	poorer flexibility higher cost poorer adhesion
chlorinated rubber (see Rubber derivatives)	greater toughness and hardness better abrasion resistance better chemical resistance faster dry	poorer solvent resistance

The influence on individual coating properties of blending alkyds with the common blending ingredients is indicated by the following:

To increase drying speed. Add nitrocellulose, vinyl polymer, phenol-formaldehyde resin, chlorinated rubber, rosin esters, and modified phenolics.

To increase hardness and mar resistance. Add phenolics, amino resins, rosin esters, chlorinated rubber, epoxies, and polyisocyanates.

To improve color and color retention. Add acrylics, amino resins (especially melamines).

To improve gloss and gloss retention. Add rosin esters, amino resins (especially melamines), acrylics.

To improve durability. Add acrylics, amino resins (especially melamines).

To improve heat resistance. Add silicones, amino resins.

Manufacture

As discussed earlier, the preparation of alkyd resins is essentially an esterification process in which the polybasic acids and polyhydric alcohols are reacted with various oils or fatty acids and modifying agents in a reaction kettle. When a fatty acid is used, the process chiefly involves direct esterification. When an oil is the fatty acid source, an alcoholysis or ester-exchange reaction between the oil and the polyhydric alcohol is usually carried out before the esterification step.

Four basic methods for manufacturing most alkyd resins are recognized: the fatty acid method, the fatty acid-oil method, the oil dilution method, and the alcoholysis method. The fatty acid and alcoholysis methods are the most important today. Many variations have been reported (35-37). Other manufacturing methods are used when necessitated by such considerations as unusual chemical or physical properties of modifiers, special characteristics required of the finished resin, or variables in processing equipment.

Fatty Acid Method. The entire charge of fatty acids, polyhydric alcohols, and dibasic acids is heated to reaction temperature (usually 210-250°C, but as high as 280°C may be used) and maintained until alkyd specifications are met. A variation in which the polyol is reacted with the dibasic acid before addition of the fatty acids gives very rapid viscosity rise, wide alkyd molecular-weight distribution, poor stability with driers, a tendency toward surface drying, and often gel formation in films.

Fatty Acid-Oil Method. The entire charge of fatty acid-oil-polyhydric alcohol and dibasic acid is added to the reaction kettle, and the temperature is raised to 210-280°C and maintained in this range until specifications are reached. Alkyds made by this method give coatings with more rapid top-drying and slower through-drying than those from the alcoholysis method. It is important to have the correct ratio of fatty acids to oil; otherwise, partial gelation ("seeds") can occur.

Oil-Dilution Method. The base alkyd is prepared by either the fatty acid, fatty acid-oil, or alcoholysis method. This alkyd is diluted with oil at elevated temperatures to the desired oil concentration. Alkyds prepared by this method usually exhibit better brushing characteristics, but produce somewhat softer coatings with poorer color retention and durability than do alkyds made by the fatty acid or alcoholysis methods.

Alcoholysis Method. A large proportion of alkyds are made by alcoholyzing triglyceride oils, such as soybean and linseed, with pentaerythritol or glycerol as the additional polyol. After redistribution of the fatty acid groups, the partial esters, which now have free hydroxyl groups, are esterified with dibasic acids such as phthalic anhydride. In comparison with the fatty acid method, the alcoholysis method gives the following differences in alkyds: higher and more rapidly attained viscosity and gelation at low degrees of esterification; and softer and slower drying coating films.

The uncatalyzed (38) alcoholysis reaction takes place readily only at 280°C or above. Acid materials (39) are relatively ineffective as catalysts. The alcoholysis of

triglyceride oils in making alkyds is usually base-catalyzed with alkali or other metallic compounds. Alkali metal hydroxides are effective as alcoholysis catalysts but tend to give alkyds of darker color and make the alkyd films more water-sensitive.

A study (40) of the base-catalyzed alcoholysis of soybean oil with pentaerythritol showed that on an equal mole basis (0.00224 mole catalyst per 1000 grams oil), lead compounds were most efficient, followed closely by lanthanum naphthenate, calcium naphthenate, cerium naphthenate, calcium acetate, and lithium salts. In most commercial alkyd preparation, sublimed litharge has been the preferred alcoholysis catalyst, since it gives faster esterification rate, equivalent color, and higher viscosity than other alcoholysis catalysts such as calcium and lithium salts. The litharge concentration usually ranges from 0.01–0.05% metal based on the weight of the triglyceride oil. For rapid and successful alcoholysis, the processing equipment should be clean and free of carboxylic materials such as residual phthalic anhydride from previous alkyd preparations, or highly acidic triglycerides.

The general alcoholysis method proceeds as follows: The oil is heated to 230–250°C, the sublimed litharge and then the polyol are added, and the mixture is reheated to 230–250°C. One way to follow the course of the alcoholysis reaction is by noting the solubility of the mixture in anhydrous methyl alcohol. The triglyceride oils are insoluble in anhydrous methyl alcohol, whereas the monoesters are soluble. When at least 2 volumes of methanol per volume of alcoholysis mixture give a clear solution, the phthalic anhydride is added and the alkyd is completed at a reaction temperature of 210–250°C to the desired specifications.

Fusion Versus Solvent Processing. Any of the four methods described above, which vary only in order of addition or source of ingredients, can be further modified in point of technique during the esterification cycle. If any of the four are carried out as described, the process is called a *fusion process*, a term which presumably signifies that the fluidity of the mass is developed by heat. The technique of adding an azeotroping liquid as an aid to removing water during simple esterification reactions can also be used in alkyd processing. When this is done, the process is referred to as a *solvent or azeotropic process*.

In the fusion process, the evolved water of esterification is vented to the atmosphere or is collected in a fume scrubber system. In the solvent process the amount and kind of solvent present (aromatic types are preferred), usually 3–10% of the batch charge, is adjusted so that a vigorous refluxing occurs at the desired esterification temperature. The vapors are condensed and collected in an automatic decanter which removes the water and returns the solvent to the reaction kettle. Aliphatic solvents are generally not used in the solvent processing of alkyds because they are poor solvents for phthalic anhydride, which can sublime and plug the reflux condenser tubes. In the solvent process, better temperature control is possible by the addition or withdrawal of solvent than by the regulation of heat put into the kettle.

In solvent processing of alkyds made by the fatty acid method, the usual procedure is to charge all the ingredients and the solvent. In alcoholysis, the solvent is withheld until after the alcoholysis is completed. The solvent is then added after the dibasic acid.

General Processing Considerations. Certain processing conditions must be observed, regardless of the technique of preparation. Thorough agitation is required to provide intimate contact of immiscible materials, such as polyol and oil, during the early phases of the reaction, and to provide a homogeneous blend during the latter

stages. Mechanical agitation is generally supplied through motor-driven propellers, paddles, or turbines at a rate providing peripheral speeds of 600–800 feet per minute.

In addition to mechanical agitation, additional mixing is provided by means of inert gas sparges. Carbon dioxide, nitrogen, or combustion gas mixtures of carbon dioxide and nitrogen are preferred. Such gases are generally introduced as a stream of fine bubbles through a perforated tubular ring below the surface of the liquid mix. Although the prime reason for an inert gas sparge is prevention of side reactions resulting from oxygen contamination (polymerization of the fatty acids and color formation), the effective removal of condensation reaction products, mainly water, also results. The inert gas rate commonly used varies from 0.005 cubic foot per minute to 0.04 cubic foot per minute per gallon charge. The higher rates are generally introduced during the late stages of the alkyd reaction to ensure optimum removal of water.

The overall consequences of mechanical agitation and inert gas sparging are more rapid reaction, more uniform molecular-weight distribution, fewer side reactions, and better alkyd colors.

In addition to the expected evolution of the water of reaction during esterification, a number of other losses, both chemical and physical, are encountered during alkyd preparation. Naturally the amount of loss depends upon the equipment, preparation, procedure, and ingredients. Low-boiling polyols volatilize, phthalic anhydride sublimes readily, polyols or other ingredients char from localized overheating, and gel particles form as a result of inadequate mixing or improper formulation. Overall losses of 3–10% during alkyd preparation have been reported (26).

In both fusion and solvent processing of alkyds, the resin reaction is stopped by dropping the batch into a jacketed tank fitted with a condenser and containing the desired solvent for dilution to the finished alkyd resin product. The cooled resin solution is adjusted to the desired resin content, filtered, and transferred to bulk shipping facilities, bulk storage, or drums.

The solvent process for preparing alkyds has the following advantages over the fusion process: alkyds of better color and polymer uniformity; higher yields owing to lower phthalic anhydride or polyol losses through condensers; lower esterification temperatures; faster esterification cycles; easier temperature control; easier cleaning of the kettle; and easier alcoholysis of subsequent batches. Although the trend is in the direction of solvent processing techniques, there will still be a considerable volume of alkyds made by the fusion process for the following reasons: (a) there is a large investment in existing plant installations; (b) certain alkyds, such as the isophthalic types, are more easily made by the fusion process; (c) investment cost is lower on new alkyd installations; and (d) safety requirements are less stringent than with solvent processing equipment.

Most new installations for making alkyds are based on the solvent process. They have both a partial and a total condenser system. The same equipment can also be used for the manufacture of unsaturated polyesters based on glycols and dibasic acids.

The partial condenser is operated to return to the reaction vessel all reactive ingredients—for example, low-boiling glycols, higher-boiling polyols, phthalic anhydride, or fatty acids. The purpose of the partial condenser is to separate these materials from the evolved water of reaction or azeotrope. The azeotrope is condensed in the total condenser and passed into a decanter which returns the azeotroping solvent to the reaction mixture. Naturally, none of these separations is absolute. Their completeness depends on the vapor pressures of the various substances. A scrubber also is used to

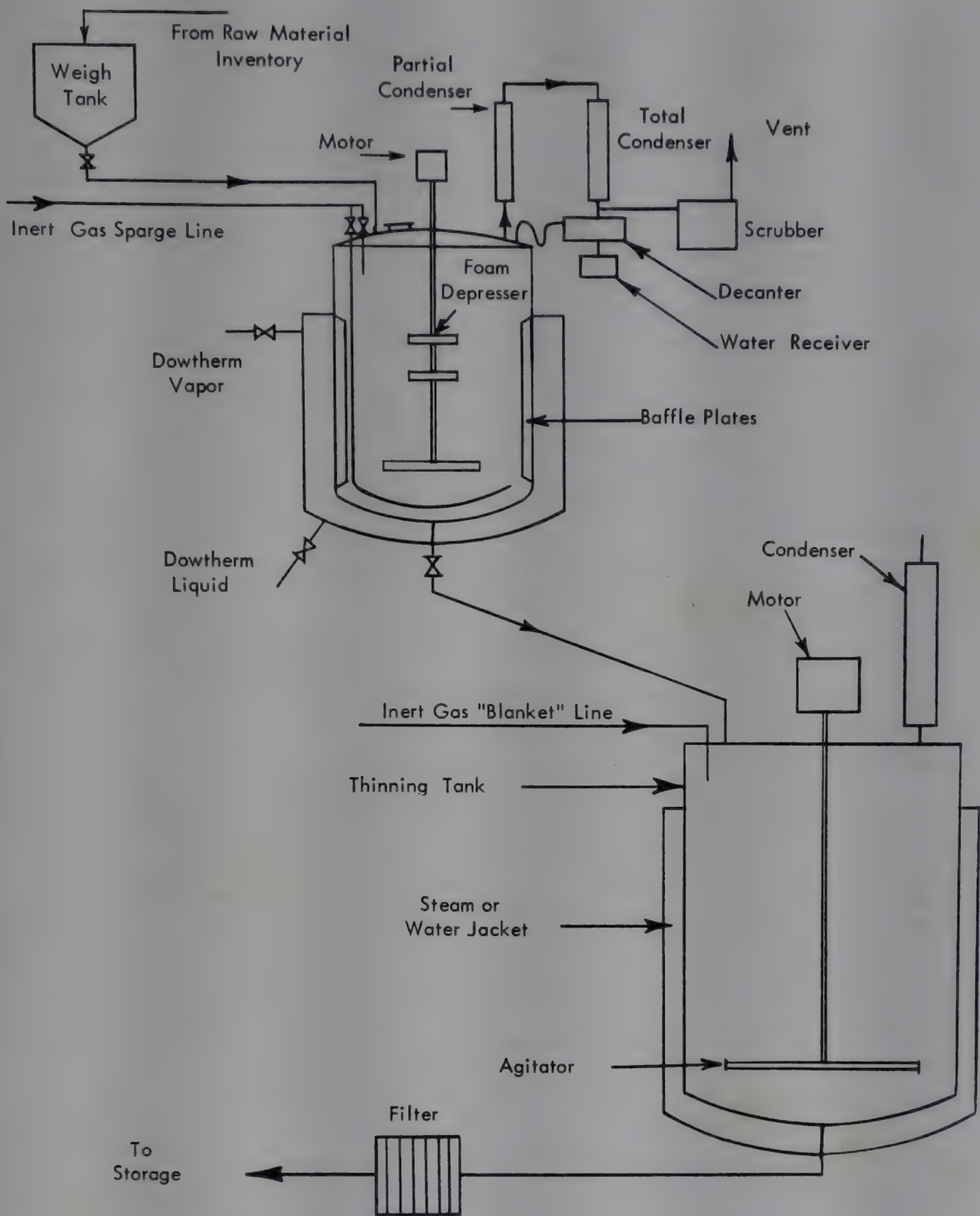


Fig. 1. Schematic diagram of typical alkyd processing plant.

purify the off-gases (consisting mainly of the sparging gases) for release to the atmosphere. Figure 1 illustrates the equipment and flow of materials.

Alkyd Equipment. The progress in alkyd resin equipment from its earliest beginnings has been recorded by Hovey (41), who discusses materials used for kettle construction, plant layouts, parts and accessories for the resin kettles, and the merits and disadvantages of different heating and cooling systems.

Most modern alkyd resin plants have the following basic equipment and facilities:

1. Tank facilities for bulk storage of liquid alkyd ingredients such as oils, fatty acids, glycerol, glycols, molten rosin, molten phthalic anhydride, vinyl monomers, and solvents.
2. Warehousing facilities and materials handling equipment for solid alkyd ingredients, such as pentaerythritol, phthalic anhydride, benzoic acid, and isophthalic acid, and for polymeric modifiers, such as epoxies, acrylics, phenolics, and rosin ester.
3. Weighing hoppers and metering devices for addition of dry and liquid alkyd ingredients.
4. Resin kettles equipped with agitation, inert gas facilities, partial and total condenser systems, solvent decanters, temperature recorders, and fume scrubbers for both alcoholysis and esterification reactions.
5. Temperature controls for direct heating systems using gas, fuel oil, or electricity, or for indirect heat transfer systems using Aroclors or Dowtherms.
6. Automatic control devices for controlling reaction temperature and pressure, inert gas flow rate, and solvent return rate, to help ensure the necessary uniformity of processing conditions.
7. Jacketed thinning tanks equipped with reflux condenser, cooling coils, agitator, and inert gas facilities.
8. Filtration equipment.
9. Bulk product storage and loading facilities for drums, tank wagons, and tank cars.
10. Warehousing area for finished products.
11. Quality control laboratory.

Most standard equipment for processing alkyd resins, especially the reaction kettle, is constructed of stainless steel alloy; types 304, 316, and 347 are the most popular. Owing to the wide variety of ingredients used in the manufacture of alkyd resins, the chemical corrosion resistance of stainless steel is a distinct advantage over most other metals. Stainless steel is further dictated by the required service life of the alkyd equipment and the need for pale colors in the completed alkyd.

Health and Safety. The manufacture of alkyd resins involves a wide variety of ingredients which, from the health standpoint, generally exhibit little or no toxicity. Reasonable precautions, such as the use of rubber or leather gloves, protective clothing, eye protection, and respiratory devices are employed in handling the various ingredients. Cleanliness and careful handling by the employees are essential. The information needed for the safe handling of alkyd ingredients can be obtained from suppliers of alkyd raw materials.

The observance of good safety practices in manufacturing alkyd resins is of utmost importance because of the volatility and flash points of the azeotroping and "thinning" solvents used. Accident prevention programs are continually stressed in the training of old and new employees. General safety in the protective coatings industry has been discussed by Jones (42).

Quality Control and Specifications

In most alkyd manufacturing plants, quality control begins with the incoming raw materials, which are purchased according to the buyer's specifications. Quality con-

trol measurements help to define the general composition of the raw materials and to detect undesirable impurities. No uniform code has been established by the industry; however, many pertinent specifications and methods for testing ingredients and solvents have been provided by the American Society for Testing and Materials (43). Raw material suppliers have also recognized the need for uniformity and provide products conforming to closely controlled specifications.

The quality of the resin is controlled during manufacture by testing in-process samples to determine reaction progress. These samples must be representative of the reaction mass at the time they are taken. Rapid cooling of the sample is required, therefore, to avoid continuing reaction.

While the basic purpose of in-process control is to guarantee product quality, such control is also used to determine reaction completion. Guideposts ordinarily are derived from tests on previous plant batches of similar alkyds. However, when the manufacturer changes his alkyd, the new formula can be calculated by any one of numerous methods (25,26,44-46). Experimental laboratory verification, often with samples of the plant lots of raw materials, is an additional safeguard.

By determining the gelation point of the alkyd, a reaction stage slightly beyond the desired point of reaction completion (see Chemical reactions), and making the tests indicated below, effective predictions of reaction behavior during large-scale processing can be made.

The in-process samples are tested for the following: acid number; viscosity of solutions of known concentrations in solvents such as mineral spirits or xylene; color of the alkyd solution; and cure time. The acid number, which is defined as the number of milligrams of potassium hydroxide required to neutralize 1 gram of the solid material, is a measure of the degree of esterification. As mentioned earlier, the alkyd formulator generally attempts to obtain an alkyd with as low an acid number as feasible, short of the gelation point. A target range of 2-5 acid number units (25,26) above the acid number of gelation will generally give an alkyd which not only performs satisfactorily on storage (no further reaction to form gel particles) and in the coating, but also can be processed without danger of gelation in the reaction vessel. Normally, the final acid number of an alkyd must also be relatively low to avoid inferior properties in the coating. The majority of alkyds manufactured have a final acid number of less than 15. Viscosity measurements in any given alkyd represent the amount of polymerization and the increase in molecular weight. These viscosities are usually measured by dilution of the resin with a known amount of solvent and comparison of a standard tube containing this solution with Gardner-Holdt viscosity tubes. This comparison involves establishing an equivalence in the time required for an air bubble to rise in a vertically held tube of the unknown sample and a control tube. The Gardner-Holdt tubes are graduated in irregular increments of viscosity and are designated by letters which range from A-5 to Z-10. The corresponding viscosities in poises are 0.00505 at A-5 to 1066 at Z-10.

The acid number and solution viscosity values are plotted against the reaction time on semilogarithmic graph paper. These curves can be extrapolated to determine the proper end point prior to actual completion. This extrapolation is extremely important, especially in dealing with alkyds containing less than 45% oil. The difference between a satisfactory short-oil alkyd and a gelled mass can be the time required to determine the acid number and viscosity. The sampling and test procedures must,

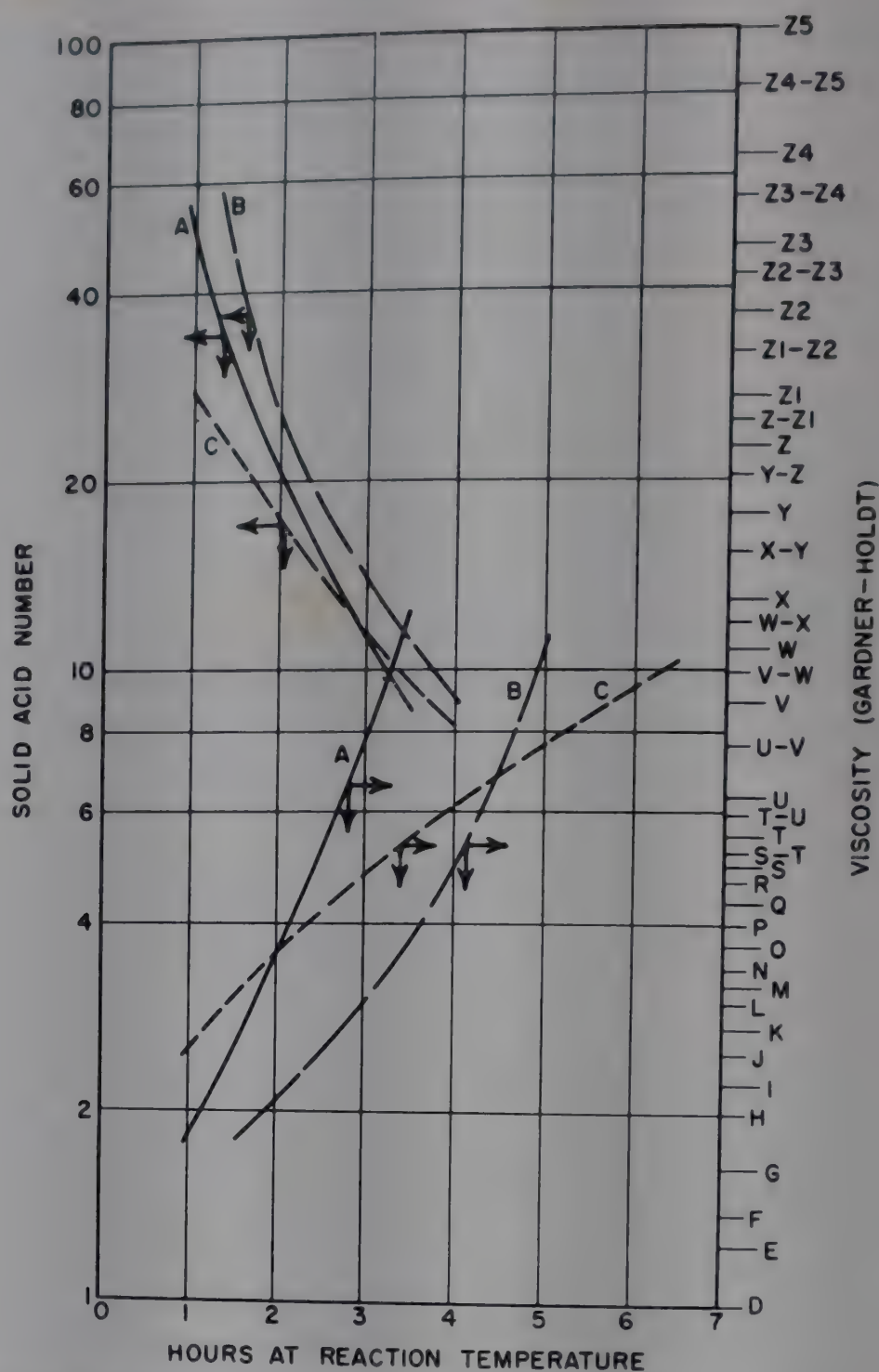


Fig. 2. Viscosity-acid number control of alkyd resins. Curve A, 37% soybean oil-pentaerythritol-ethylene glycol-phthalate alkyd; curve B, 54% soybean oil-pentaerythritol-phthalate alkyd; and curve C, 63.5% soybean oil-pentaerythritol-phthalate alkyd.

therefore, be rapid and accurate, and prior indication of completion of the alkyd reaction is important.

Figure 2 shows typical viscosity and acid number versus time plots for three alkyds of varying oil length. The steep rise in the viscosity-time curve for the 37% oil alkyd is pertinent to the problem discussed in the previous paragraph. The curvature of the lines shown, however, illustrates the potential inaccuracy of the extrapolation to reaction completion as described above. An alternate plot (25) of acid number versus reciprocal of the viscosity in poises generally results in a straight line which can be readily extrapolated to give the acid number at the gelation point. This method is useful for establishing a desirable range for alkyd acid number at the end point of processing and helps to determine whether or not the alkyd has been properly formulated. However, the technique cannot be applied where reaction time is a con-

sideration, and consequently, the type of charting shown in Figure 2 is used for manufacturing operations.

Cure time is also a measure of the degree of polymerization. The test is run by placing a drop of alkyd on a metal plate held at 200°C and determining the time required for solidification (gelation) of the alkyd (to a film). Solidification is estimated as that point at which the alkyd cannot be cut manually with a pointed nail. Although the test is highly subjective, the operator can become quite proficient and obtain replication. The shorter the time of solidification, the closer the alkyd is to the gel point. Consequently the method serves as a check against the viscosity-acid number methods. Cure time values below 10 seconds generally indicate unstable alkyds (44).

Color measurements are generally made by comparison of the same sample used for viscosity (see above) with Gardner 1933 Color Standards. The chief value of in-process color measurement is to detect impurities or faulty processing conditions, such as a dirty reaction kettle or inadequate oxygen exclusion. The color of the final alkyd is highly important because of possible interference with the color of the paint or other coating which is prepared from the alkyd.

The final step in quality control is an analysis of the finished resin for product quality. This step can include specifications for such constants as acid number, solution viscosity, solution softening point, dilution characteristics, and percent solids. These physical constants are not a measure of the alkyd resin's performance characteristics, but are valuable in quality control of successive batches of the same resin. If two resins made from the same raw materials under the same process conditions have the same physical constants, they generally will provide equivalent performance in any coating application. Consequently, these measurements provide a fairly reliable short cut to the performance of the paint or other coating, which ordinarily would require lengthy testing to establish its durability on exposure.

Because the buyer of an alkyd resin is not aware of its ingredients, his specifications often include, in addition to tests of quality control, a significant number of requirements and tests of the ingredients used. These more comprehensive specifications are required to shorten the time that would be required to certify the quality of each lot of alkyd as it pertains to the performance of the coating in which it is used. Because such a wide variety of ingredients can be combined to give the same values for such quality-control specifications as viscosity, acid number, cure time, and solids content, the buyer cannot be assured of quality performance in paint exposure unless he also knows the exact amount and kind of ingredients used. The objective of these specifications is the definition of performance characteristics of the alkyd in a practical and economic manner.

To identify an alkyd thoroughly requires extensive analytical testing which only large-volume purchasers can afford. Consequently, purchasers of small amounts of alkyd must depend on the competence and reliability of their suppliers. Although no uniform specification code has been developed, the American Society for Testing and Materials (43) has published a series of recognized methods and procedures for determination of alkyd ingredients and performance of coatings from the alkyd.

A good example of the types of information of concern to buyers can be found in Federal Specification TT-R-266a, September 21, 1955. Included in this specification are requirements and methods to determine the following: amount and kind of fatty acid; amount and kind of polyol; amount of phthalic anhydride; amount and kind of

solvent; amount of metallic constituents; color; viscosity requirements at varying solvent concentrations; amount of alkyd resin; coating behavior—drying time and water resistance; and compatibility of alkyd with oils, pigments, and resins.

Uses

Alkyd resins are used in both clear and pigmented, industrial- and trade-sales coatings to protect and decorate a wide variety of substrates. Industrial coatings or finishes generally are applied during the manufacturing process of the item which they cover. Often they are specifically formulated to meet both conditions desired for their application and the end use of the article of manufacture. Trade-sales finishes are stock-type commodities usually distributed through wholesale or retail channels.

Industrial finishes include primers and topcoats for stoves, refrigerators, washing machines, automobiles, machinery, wood and metal furniture, electrical equipment, and printing inks.

Trade-sales finishes can be classified as follows:

- A. Interior Architectural Finishes
 - 1. Alkyd flats
 - a. Wall paints
 - b. Wall primers and sealers
 - 2. Semigloss enamels
 - 3. Gloss finishes
 - a. Gloss paints
 - b. Painters' enamels
 - c. Gloss enamels
- B. Exterior Architectural Finishes
 - 1. Enamel undercoat
 - 2. Enamel topcoat
- C. Miscellaneous Trade-Sales Paints
 - 1. Porch floor and deck finishes
 - 2. Chemically resistant paints

As indicated previously, the kind and amount of oil or fatty acid in the alkyds determine to a large extent their end-use applications and have an important effect on such coating properties as the following: speed of surface dry, speed of through-dry, gloss and gloss retention, color retention, gasoline and water resistance, adhesion, flexibility, hardness, and marproofness. Thermoplastic film-formers—for example, nitrocellulose, ethyl cellulose, chlorinated rubber, and vinyls—contribute to coating properties such as fast dry, chemical and solvent resistance, heat-sealing, easy spot repair, and, with the right application procedures, no lifting on recoating. Unfortunately, in coating uses these materials alone have drawbacks of poor adhesion, low solids at application viscosity, low coating-depth film, usually high shrinkage, usually poor flexibility, fair gloss, and high cost. The modification of these thermoplastic film-formers with alkyd resins will frequently correct these deficiencies.

Short-Oil Alkyds. The short-oil alkyds with 30–45% fatty acids (more than 35% phthalic anhydride) may be divided into *nondrying* and *drying* types. They have high viscosities and require strong solvents such as xylene; coatings made from them are generally applied by spraying or dipping.

The short-oil nondrying alkyds contain coconut, hydrogenated coconut, castor, pelargonic, or similar saturated fatty acids. They are used as plasticizers in nitrocellulose lacquer and in baking enamels combined with amino (urea and melamine) resins. As plasticizers, resins of this type contribute the necessary properties of adhesion, flexibility, durability, and color retention for automotive and other fast-drying industrial finish applications. The nondrying alkyd-amino resin baking enamels yield very hard, tough finishes for automobiles, refrigerators, washing machines, home freezers, and other metal finishing uses. Such enamels are outstanding for retention of color and gloss, and are relatively impervious to food stains, soap, water, and mild acid and alkali solutions.

The short-oil drying alkyds contain tall-oil fatty acids, soybean, cottonseed, dehydrated castor and linseed oils, or fatty acids. These short-oil-drying alkyds have fast set, fair air-dry, fair flexibility, good adhesion, good durability, good gloss and gloss retention, fair-to-good color retention, and rapid baking cycles. These alkyds have a broad base of utility in industrial baking finishes of all types. When baked, short-oil-oxidizing alkyds are more durable than the longer oil-oxidizing alkyds and generally possess better hardness, marproofness, gloss, and color retention. They are used in metal cabinet, venetian blind, automotive, toy, can and cap coatings, and washing machine finishes either alone or in amino resin blends. They are also used as metal primers. These short-oil-drying alkyds modified with acid-catalyzed urea resins have found successful application in forced-dry, wood furniture finishes.

Medium-Oil Alkyds. The medium-oil alkyds with 46–55% oil (30–35% phthalic anhydride) are the most versatile of the alkyd family and can be applied by brush, spray, or roller coat. Some of these resins can be used in baking finishes with amino resins. The baking schedules are longer and their color and color retention are inferior to short-oil alkyds containing the same type of oil modifier. The medium-oil-oxidizing types give excellent gloss, durability, and flexibility; set time is short and through-dry to hardness is fairly rapid. These medium-oil alkyds find use in air-drying or baking enamels, maintenance paints, metal decorative coatings, automotive refinish enamels, architectural enamels, farm implement and machinery paints, freight car finishes, furniture finishes, metal primers, porch and deck paints, roller-coating finishes, and toy enamels.

Long-Oil Alkyds. The third category of alkyds has 56–70% oil modification and 20–30% phthalic anhydride. These alkyds are soluble in aliphatic (mineral spirits) solvent, and are compatible with many oils and oleoresinous vehicles. They have good brushing properties, and find wide applications in structural steel finishes, marine paints, chlorinated rubber finishes, interior and exterior architectural enamels, and as aluminum paint vehicles and trim and trellis paints. They can be used to fortify linseed oil vehicles used in house paints and also as fortifiers for latex-paint systems.

These long-oil-drying alkyds have good overnight dry, and give flexible films of good gloss, gloss retention, and excellent durability. Their hardness, toughness, and abrasion resistance are inferior to the medium-oil alkyds.

Very Long Oil Alkyds. The fourth category of alkyds has greater than 70% oil content and less than 20% dibasic acid. They are soluble in mineral spirits solvent and compatible with many oils and oleoresinous vehicles.

Very long oil alkyds are the slowest drying, and have good brushing properties and durability. These types of alkyds are used in printing inks and exterior house and shingle paints, as tinting base vehicles, and to modify latex emulsions.

Economic Aspects

Production statistics for alkyd resins from 1950–1960, as classified by the U.S. Tariff Commission, are given in Table 4. In view of a number of changes in reporting

Table 4. Production Statistics, in Thousand Pounds, for Alkyd Resins^a

Year	Total alkyds	Phthalic alkyds	Nonphthalic alkyds	Amount in noncoating applications ^b
1950	401,966	332,983	68,983	not separated
1951	440,585	368,352	72,233	not separated
1952	431,266	357,177	74,089	9,059
1953	466,500	390,527	75,973	
1954	453,601	382,367	71,234	
1955	543,215	455,994	87,221	
1956	473,846	392,415	81,431	
1957	528,537	439,870	88,667	
1958	502,590	416,837	85,753	15,727
1959	559,961	472,775	87,186	24,954
1960	556,400	464,724	91,676	35,121

^a U.S. Tariff Commission, *Synthetic Organic Chemicals*, United States production and sales for years 1950–1960 inclusive.

^b Figures reported for the years 1953–1957 are not considered meaningful and, therefore, are not shown in the table.

such statistics, figures prior to 1957 are not considered accurate. However, the data do indicate that alkyd production has essentially leveled out. In recent years competitive materials, such as polymer emulsions used in latex paints, have taken markets, especially in interior finishes, from alkyds. Any substantial growth appears dependent on new scientific advances in alkyd formulation or their penetration into new use areas. The slowdown in alkyd growth also appears reasonable in view of the slow growth in the use of protective coatings. Protective coatings appear to be maintaining, at best, a growth proportional to the population increase, and they serve as a market for almost 95% of the alkyds made. No statistics are available to define the production or use of alkyds by oil content, although long-oil alkyds are believed to be in the large-volume category. Nor is there reliable published information on the relative quantities of drying and nondrying coating alkyds produced or used. Unpublished estimates of the Hercules Powder Company indicate that about 10% of the alkyds made are nondrying. No complete estimates of the amounts of various monobasic fatty acids which become alkyd components are available. Pattison (47) estimates from Bureau of the Census statistics that, excluding tall-oil fatty acids, about 35 million pounds per year of unsaturated vegetable acids were used in alkyds from 1954 through 1957, or about 8–9% of the total alkyd production. Such information is no longer compiled by end use by the Bureau of the Census. Extrapolations of Pulp Chemicals Association data (48) indicate that 50–55 million pounds of tall-oil fatty acids were used in alkyds in 1961. Whether this usage has been at the expense of either unsaturated vegetable fatty acids or oils cannot be stated because of the lack of comparable statistics for the year. Moreover, the total amount of monobasic fatty acids in alkyds that is derived from conversion of oils during alkyd preparation is not known. Presumably one reason is that this use of oils is not catalogued because it represents a very small fraction of the oil market. However, on the assumption that the average monobasic fatty acid con-

tent of alkyds is 55%, the total monobasic acid use would be about 250,000,000 pounds in 1960. Monobasic acids from oil sources then might be as low as 160,000,000 pounds in 1960. Errico (49) has estimated that 65 million pounds of glycerol and about 60 million pounds of pentaerythritol were consumed in alkyds in 1960.

There is relatively little exporting of alkyd resins from the United States. Exact information on alkyd production of other countries is equally difficult to develop because of the different definitions for alkyds. However, the following estimates, in thousand pounds (based on unpublished data of the Hercules Powder Company), are available for 1960:

United Kingdom	110,000	Italy (1959)	31,000
Western Germany	130,000	Australia	27,000
Netherlands	40,000	France	20,000
Japan	40,000		

In a report of United States trade-sales and industrial paint consumption, Bigelow (50) has made an attempt to estimate the amount of each type of coating vehicle used in these categories. He points out the type of inconsistencies which may be encountered. For example, although paint consumption presumably was lower in 1957 than in 1956, alkyd production appears to rise 20%. To avoid further inconsistencies, Bigelow has restricted his estimated paint consumption by resin-vehicle types to years since 1953. Table 5 summarizes these data, and shows that alkyd resins are used in the largest proportion of both trade-sales and industrial paints.

Table 5. Trade-Sales and Industrial Paint Consumption

Type	Paint consumption, mil gal						
	1953	1954	1955	1956	1957	1958	1965 ^a
<i>Trade-sales paints</i>							
total	282	276	296	309	310	304	430
interior							
alkyds	66	62	65	64	62	57	75
latex	30	34	46	50	55	65	130
exterior							
oil-base	102	96	105	114	106	100	225 ^b
all other	84	84	80	81	87	82	
<i>Industrial-sales paints</i>							
total	381	343	404	394	390	350	450
straight alkyd	201	174	203	194	194	179	200
alkyd blends with							
amino resins	54	50	77	75	72	60	80
lacquers	62	57	68	64	60	55	65
others ^c	64	62	56	61	64	56	105
phenolics		31	36	36	36	32	30
polyvinyl chloride		13	13	15	16	16	20
epoxies		5	7	8	12	13	23
others		2	2	2	2	3	32

^a Extrapolated values for 1965.

^b These include epoxy, phenolic, polyvinyl chloride, acrylic, urethane, and polyester-based materials.

^c This does not add up to total owing to overlapping of categories.

Future Prospects

Important factors which will help decide the future of alkyd resins are costs, new applications, and formulations of new types of alkyds with improved performance. One of the most important reasons that alkyd resins should continue to hold their own is economy. The cost of alkyd resins depends on two factors—raw material costs and processing costs. Efficiency in processing is such that it contributes little to the final costs, but further reductions are possible if success comes to present efforts to develop continuous alkyd production methods. The raw material picture is also favorable. Phthalic anhydride, the backbone of alkyd resins, is being produced today in large volumes, and overcapacity exists in the industry. This has led to a reduction in price of phthalic anhydride to that of the early forties. The low cost of ingredients, such as tall-oil fatty acids, and price reductions in polyhydric alcohols should keep the alkyds competitive with other protective coating vehicles.

Research departments of many major alkyd manufacturers and their raw material suppliers are engaged in intensive research on alkyds and new coating materials and formulations. Successful culmination of these research undertakings should produce a growth in the new materials, but a corresponding decline in some of the old coating vehicles.

The major lines of investigation now being carried out in the alkyd coating field include the following:

1. Improvement in corrosion prevention and in solvent resistance of coatings by combining alkyds with epoxies and other crosslinking polymers.
2. Water-based coatings, both water-dispersible and water-soluble types (51). Highly effective water-based alkyds would be expected to enjoy large markets. One problem involves finding a material which functions like a latex paint on inside walls and on exterior wood surfaces. Another important problem is the formulation of water-based alkyds that will not corrode metal for use in industrial finishes.
3. Solventless coatings. The removal of solvent or dispersing medium from paints, thus producing coatings with 100% solids, has been an objective with which the industry has been concerned for many years. A breakthrough in this field would open up new horizons for alkyd paints.

Raw materials for alkyds that are being considered include the following: trimellitic anhydride, polyethylene glycols, amino hydroxy compounds such as 2-amino-2-methyl-1-propanol, isocyanates, allyl ethers of pentaerythritol, styrene-maleic anhydride resins and dimer acids and polyamides from them, epoxies, and modified oils.

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ALKYL HALIDES. See Bromine compounds; Chlorocarbons and chlorohydrocarbons; Fluorine compounds, organic; Iodine.

ALKYL PHOSPHATES. See Phosphoric acids and phosphates.

ALKYL SULFATES. See Sulfuric and sulfurous esters.

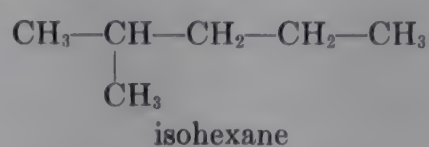
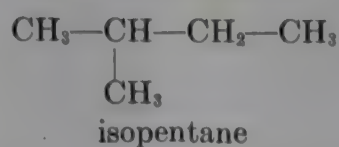
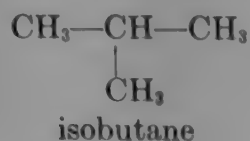
ALKYLATION

Alkylation can be described as the addition or insertion of an alkyl group into a molecule. Significant changes in chemical and physical properties can be brought about by alkylation, and the process is often considered as a direct means of imparting new or improved qualities to a compound. Consequently, alkylation has been and still is widely investigated and practiced as a means of fitting molecules for definite functions; these products are then used directly or as intermediates for further processing.

Alkylation reactions are diverse in nature. Thus there is no inclusive or universal method of conducting alkylations. The production of each compound, or type of compound, must be considered by the manufacturer with full consideration of numerous factors, including chemistry, engineering, and economics. Each alkylation reaction is subject to its particular requirements as to free-energy change, equilibrium, heat of reaction, rate of reaction, equipment, catalyst, safety, etc. This discussion selectively considers types of compounds as to methods of preparation, the chemistry involved, and some of the engineering aspects of a few commercial processes.

Nomenclature. The nomenclature used in this article is a compromise between strict IUPAC nomenclature and usages current in the petroleum industry.

"*Iso.*" The prefix "iso" (which is not used in the IUPAC system) is here used in two senses: (1) a narrow, strict sense, in which it denotes one methyl group on the next-to-terminal carbon atom (and no other branches), as in



and (2) a general, looser sense in which it means "branched chain." Thus "isoparaffin" is synonymous with "branched-chain paraffin."

Saturated Hydrocarbons. Expressions such as "hexanes," "heptanes," "octanes" are subject to ambiguity. In the IUPAC system the 6, 7, and 8, implied by the Greek derivations of these names, refer to the number of carbon atoms *in the longest straight chain*. But these words have long been used with the implied numeral referring to the *total number of carbon atoms*. Thus in this article, following common practice in the petroleum industry, the terms "hexanes," "heptanes," etc, are synonymous with "C₆ saturates" and "C₇ saturates," etc.

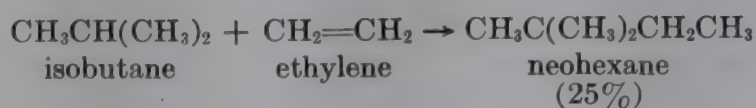
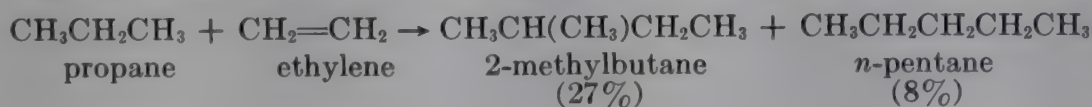
Unsaturated Hydrocarbons. The above ambiguity does not arise here, because the IUPAC has provided the termination "ene" to replace the termination "ylene." Thus "butenes" refers to monounsaturates with four carbon atoms in the longest straight chain; "butylenes" denotes monounsaturates with a total of four carbon atoms. "Butenes" therefore refers to 1-butene and 2-butene (if substituted butenes are excluded); "butylenes" refers to these two plus isobutylene (methylpropene). "Pentenes" denotes 1-pentene and 2-pentene; "pentylenes" can be used when it is required to denote these plus branched-chain C₅H₁₀ unsaturates. Similarly with "hexylenes," "heptylenes," etc.

Alkylation of Paraffins

The alkylation of paraffins can be carried out either thermally or catalytically.

THERMAL ALKYLATION

The thermal or noncatalytic alkylation of a paraffin with an olefin is carried out at high temperatures (about 500°C) and pressures (3000–6000 psi) with a contact time of about 5 minutes (1,2). Under these conditions, both normal and isoparaffins can be brought into reaction as indicated by the following examples and yields:



In this process, a free-radical mechanism is operative. The free radical derived from the paraffin adds to the olefin, followed by a chain transfer reaction with the paraffin to complete the cycle (3). The free-radical reactions can be instigated by chain initiators (4), and the use of halogen-containing reaction modifiers can increase the yield of alkylate (5). The addition of an ethyl halide to the isobutane–ethylene

reaction at 400°C increases the yield of neohexane (2,2-dimethylbutane) to 70% (5).

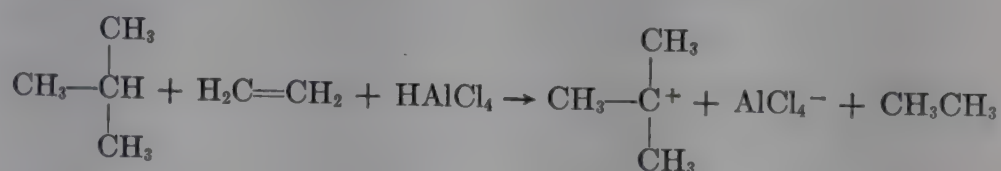
CATALYTIC ALKYLATION

The catalytic alkylation of paraffins involves the addition of an isoparaffin containing a tertiary hydrogen to an olefin. The process is used by the petroleum industry to prepare highly branched paraffins mainly in the C₇ to C₉ range, which are high-quality fuels for ignition engines. The overall process as to chemistry is a composite of complex reactions, and consequently a rigorous control of operating conditions and of catalyst is needed to assure predictable results. The process conditions required and the product composition depend on the particular hydrocarbons involved as illustrated below by the reactions of isobutane with ethylene, with propene, with the butenes, and with isobutylene (3,6,7).

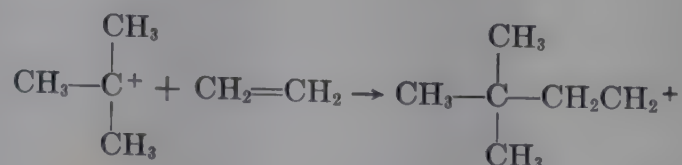
Ethylene. In alkylation with ethylene, aluminum chloride, promoted by either hydrogen chloride or ethyl chloride, has been found the material most suitable for both catalytic activity and plant operation. The halide in use forms a fluid sludge composed of highly unsaturated hydrocarbons complexed with aluminum chloride (optimum results with 13 to 17 wt % aluminum and 42 to 52% chlorine) (8). The contacting of an ethylene-isobutane mixture (1 and 4 moles, respectively) at 60°C with the sludge catalyst and ethyl chloride gives an alkylate containing 80.7 vol % of hexanes, composed of approximately 92% 2,3-dimethylbutane and 7% 2-methylpentane; 12 vol % octanes, mainly 2,2,4-trimethylpentane; and minor amounts of other materials. The formation of these products is best explained by postulating a chain mechanism with some form of a carbonium ion or cation as chain intermediates. These intermediates can be pictorially represented as cations, although the anion involved is also important.

Three steps can be considered in the sequence:

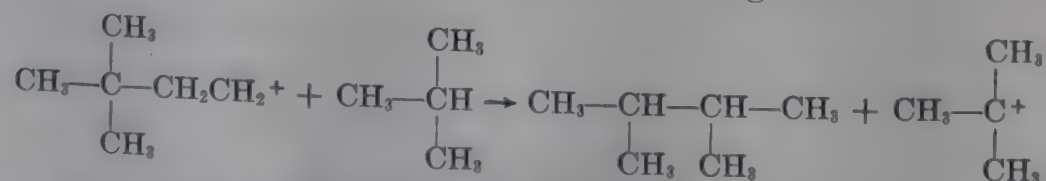
1. Formation of the *t*-butyl cation by some step such as



2. Addition of cation to ethylene

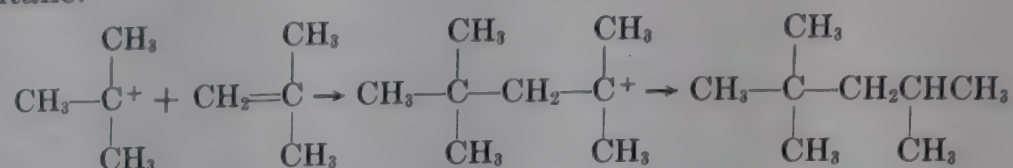


3. Transfer with isobutane and simultaneous rearrangement



Step 1 is responsible for the initiation and consequently proceeds to a minor extent. The rearrangement in step 3 probably involves stabilization of the primary carbonium ion to some form of a secondary or tertiary carbonium ion, in the latter case forcing the shift of a methyl group.

Isobutylene. The octane obtained from alkylation with isobutylene at low temperature (-25°C) with hydrogen fluoride is that theoretically anticipated, 2,2,4-trimethylpentane.



At higher temperatures with either sulfuric acid or hydrogen fluoride, the product contains, in addition, 2,3,3- and 2,3,4-trimethylpentane, besides pentanes, hexanes, and heptanes.

VARIABLES

The alkylation with propene and butenes is conducted commercially using either sulfuric acid or hydrogen fluoride as catalyst. Ethylene alkylation (thermal or catalytic) is not reported as being conducted on a commercial scale at the present time. Alkylations involving high-molecular-weight olefins and isoparaffins (over C_5) are not attractive, partly because numerous side reactions (for example, hydrogen transfer) take place. The octane rating of an alkylate depends on a number of factors, but generally is in the range 90–95 clear, F-1 (see Fuels). The alkylate composition is dependent to a large extent not only on the olefin charge stock but on operating conditions; a few of the variables are as follows:

(a) The catalysts become diluted with highly olefinic hydrocarbons and decrease in activity. Sulfuric acid concentrations are maintained at about 90%; hydrogen fluoride concentrations of 80–90% are common. Product quality decreases with a further decrease in acid concentration, particularly in the case of sulfuric acid. The optimum acid concentration with hydrogen fluoride is dependent on the reaction temperature; lower temperatures give improved product quality.

(b) With sulfuric acid, the product quality is improved with reduction in temperature to the range 0 – 10°C . A suitable temperature control can be obtained by evaporation of the hydrocarbon reactants at the site of reaction. With hydrogen fluoride the process is less sensitive to temperature, and temperatures of 0 to 40°C can be used. Some form of heat removal is essential, because the heat of reaction is approximately 600 Btu per pound of butenes.

(c) In order to prevent polymerization of the olefin as charged, a large amount of isobutane is present in the reaction zone. Isobutane-to-olefin molar ratios of 8:1 are common, but side reactions can be suppressed more effectively by use of larger ratios (up to 14:1).

(d) The alkylation reaction depends on a two-phase system, with a low solubility of the isobutane in the catalyst phase. In order to ensure intimate contact of reactants and catalyst, efficient mixing with fine subdivision must be provided. This latter factor is of importance when sulfuric acid is the catalyst because the solubility of isobutane in it is particularly low.

(e) Purity of charge stock is a factor in catalyst consumption and formation of high-boiling oils. Provisions must be made for proper pretreatment to remove sulfur compounds and water.

The commercial design and engineering features have been described for both hydrogen fluoride (9) and sulfuric acid plants (10). Figures 1 and 2 represent schematic plant flows for alkylation units with both catalysts.

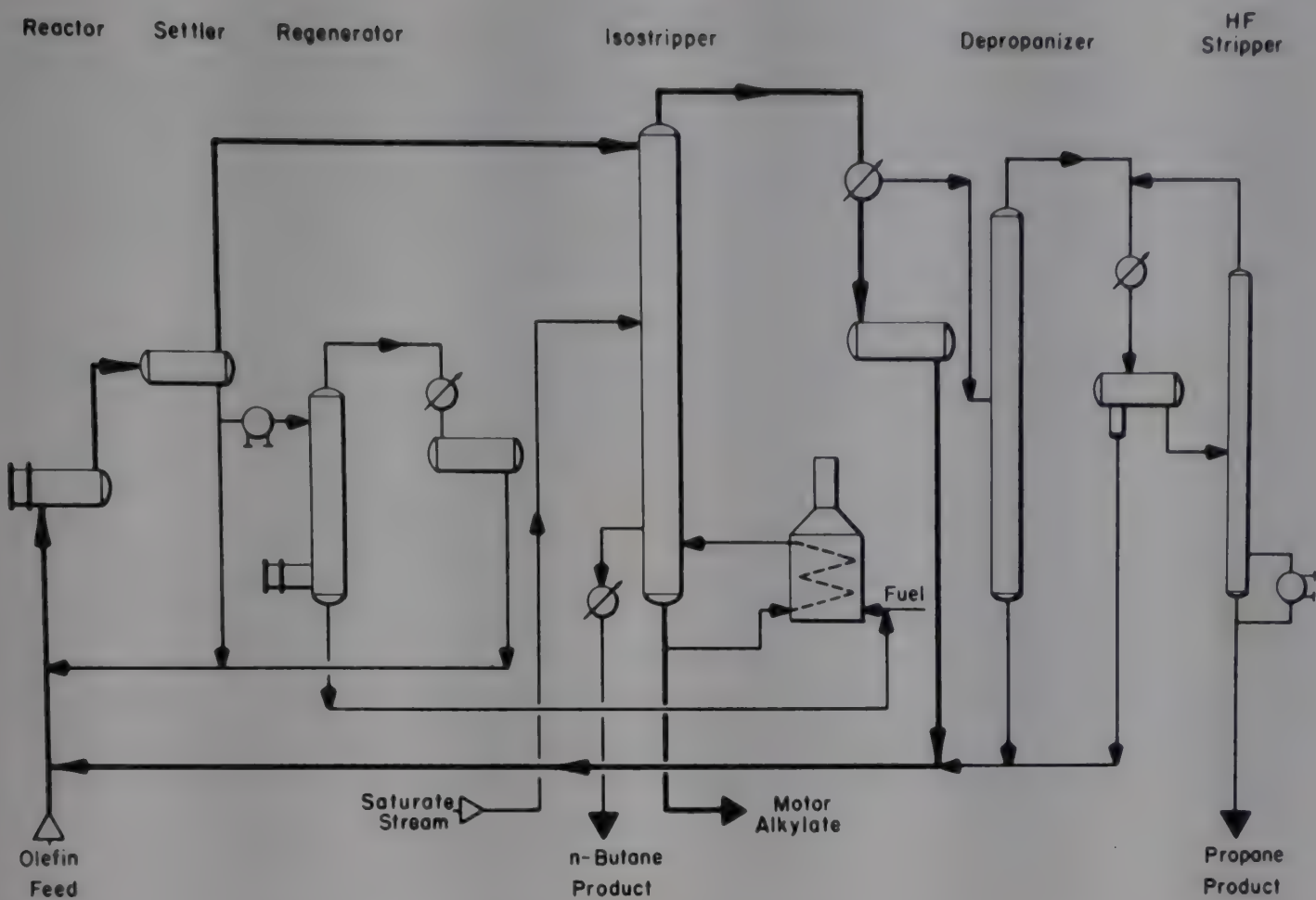


Fig. 1. A hydrogen fluoride alkylation unit.

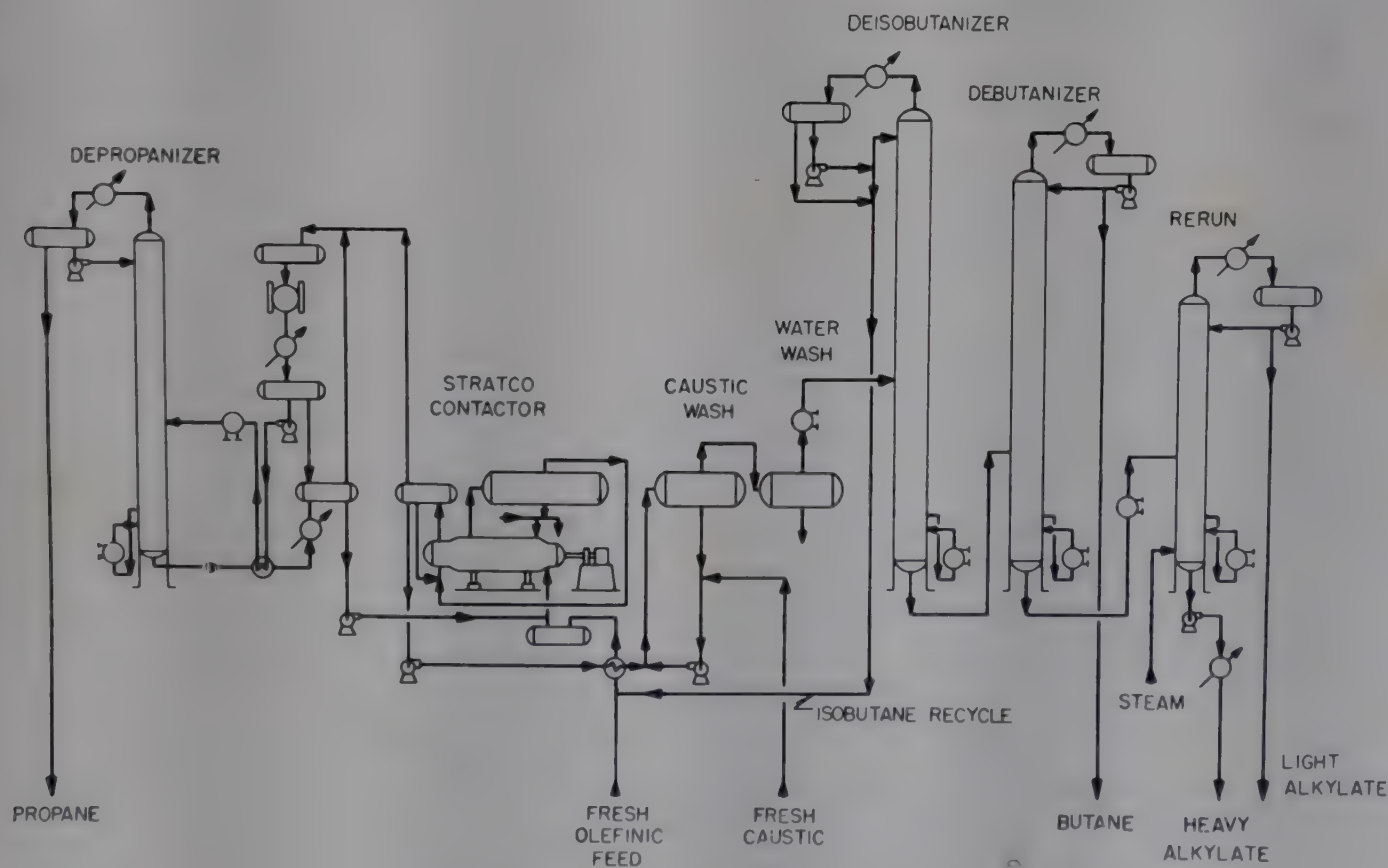


Fig. 2. A sulfuric acid alkylation unit.

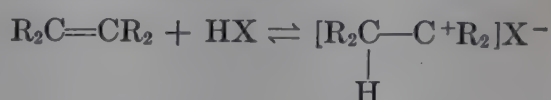
Alkylation of Aromatic Hydrocarbons

The attachment of an alkyl group to an aromatic hydrocarbon is of importance because the products have varied applications and consequently are manufactured in large volume. In many cases the alkylation can be carried out with olefins, alcohols, halides, ethers, or any olefin-producing reagent. However, for practical reasons, the alkylating reagents most commonly used are the olefins, which solely will be considered here.

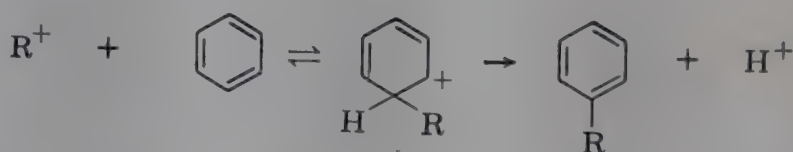
Substitution by an alkyl group can occur by attacking the aromatic hydrocarbon with a cation (carbonium ion), a neutral fragment (free radical), or an anion (carbanion).

ACID-CATALYZED (CARBONIUM ION) ALKYLATION

The interaction of an olefin with an aromatic hydrocarbon in the presence of a suitable acid-type catalyst is a direct and convenient means of alkylation. This process is an example of electrophilic substitution. The attacking species is a carbonium ion, formed from the olefin by addition of a proton from a protonic acid (sulfuric acid, hydrogen fluoride, phosphoric acid), or by a Friedel-Crafts type of catalyst (aluminum chloride, boron fluoride).



The X represents an anion—for example, SO_4H^- , AlCl_4^- . The resulting carbonium ion (represented below as R^+), an electron-deficient species, adds to an electron-rich locale of the aromatic ring. The intermediate formed, which has been described as involving a sigma-complex (11), splits off a proton to give the alkylated benzene, and a regenerated proton.



In selecting a suitable alkylation process, the overall reaction can be considered as composed of two steps:

1. Formation of the carbonium ion from the olefin; this process is controlled by the nature of the specific olefin and the nature (including activity) of the catalyst. Ethylene is the most difficult of the lower olefins to bring into reaction and catalysts such as promoted aluminum chloride or stringent conditions (elevated temperature) are used; catalysts such as sulfuric acid and hydrogen fluoride are generally not suitable. The lower olefins containing a tertiary carbon atom such as isobutylene, can readily be brought into the alkylation reaction, but as the molecular weight increases (to octenes and higher), this readiness for alkylation often wanes and side reactions may predominate.

2. The carbonium ion will preferentially attack those nuclear positions on the benzene ring where electrons are most available. Thus, the presence of a substituent on the ring can alter this electron availability by two methods, described by Ingold (12) as involving an inductive mechanism and a conjugative mechanism. For this reason, the methyl group in toluene favors electrophilic substitution; a chlorine

substituent makes substitution more difficult; and a nitro group practically excludes substitution by an alkyl group.

Ethylbenzene. The alkylation of benzene with ethylene is the main source of ethylbenzene (see Styrene). Three processes, all of which yield conversions of benzene and ethylene greater than 92%, are available for commercial-scale operation. The oldest process uses aluminum chloride promoted by hydrogen chloride as catalyst (13–15). The alkylation reaction is run at a temperature of 93°C, at pressures near atmospheric, and with the catalyst in the form of an olefin–aluminum halide complex. A considerable amount of various polyethylbenzenes is formed, of which the greater portion is transalkylated with benzene over the same catalyst under more vigorous conditions. The ethylene component of the charge generally contains a high concentration of olefin—90% and higher.

The alkylation can also be carried out over a solid bed type of catalyst, prepared from kieselguhr and phosphoric acid (16). The ethylene charge is an impure stream, in this case containing 29% ethylene. The alkylation is conducted at a temperature of 200–250°C, a pressure of 500–1000 psi, and a benzene-to-ethylene molar ratio greater than 5. The diethylbenzenes formed are not recycled for transalkylation.

A recent process, trademark Alkar, has been in commercial operation. The solid-type catalyst, at present undisclosed, is capable of transalkylating the polyethylbenzenes. This system is particularly effective with gas streams containing a low concentration of ethylene (10% and less), operating with high ethylene and benzene efficiencies (17).

Cumene. Cumene (isopropylbenzene) can be prepared conveniently by the alkylation of benzene with propylene. For use as an intermediate in phenol manufacture (see Phenol), a product of low olefin content is required; a bromine index (grams of bromine per 100,000 grams of cumene) of less than 200 is desired. To fill this requirement, polymerization to the propylene trimer must be kept low. The alkylation can be conducted in the presence of either sulfuric acid or a phosphoric acid type of catalyst (13). Phosphoric acid can be employed either in liquid form on a

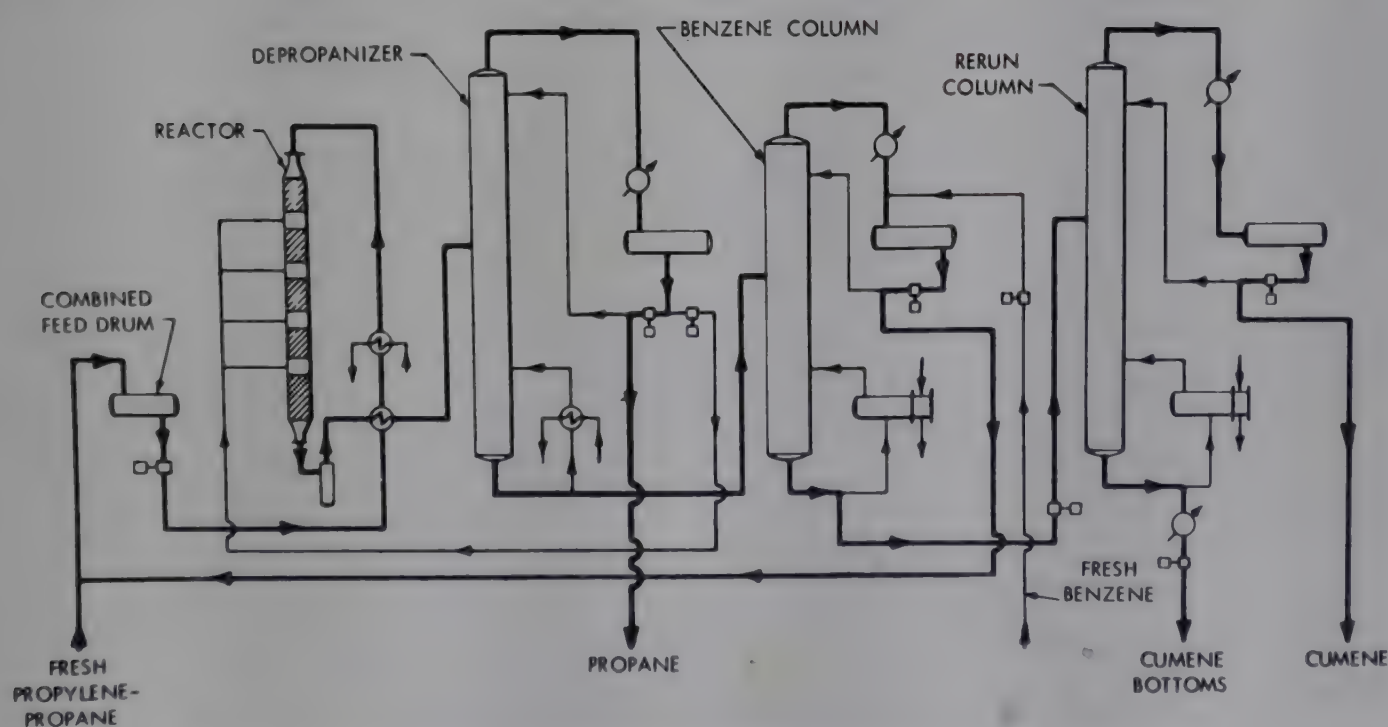
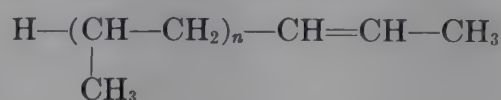


Fig. 3. A cumene alkylation unit employing solid phosphoric acid catalyst.

wetted support, or incorporated in a solid pelleted form by interaction with kieselguhr. The latter type of catalyst is being employed almost exclusively in commercial plants. Figure 3 is a flow diagram of a cumene plant using a solid-type phosphoric acid as catalyst. (See Cumene.)

Butylbenzenes. Both 1- and 2-butene give *sec*-butylbenzene upon alkylation of benzene; isobutylene gives *t*-butylbenzene. However, proper selection of catalyst and operating conditions must be made to avoid isomerization (18). The butylation of benzene is not carried out on a commercial scale in the United States.

Dodecylbenzene. The alkylation of benzene with higher molecular weight olefins in the dodecene range gives a product called "detergent alkylate." This is subsequently sulfonated and converted to a detergent (see Surfactants). Benzene is the only aromatic alkylated at the present time to produce detergent alkylate. The olefinic charge is a mixture of olefins prepared by the polymerization of propylene over a phosphoric acid catalyst (see Olefin polymers; Propylene). This olefin mixture, in the 180–235°C boiling range and prepared in the presence of an acid catalyst, theoretically should contain the following structure:



Actually, it is a mixture of branched-chain olefins of varying size and structure. Butene polymers of the same number of carbon atoms cannot be used satisfactorily because depolymerization takes place to produce appreciable amounts of lower boiling alkylbenzenes.

Three catalysts can be used to achieve alkylation—hydrogen fluoride, promoted aluminum chloride, and sulfuric acid (15,19,20). The catalyst in the case of hydrogen fluoride is recycled and reused, whereas reuse is not attempted with aluminum chloride. The hydrogen fluoride and sulfuric acid processes give maximum yields at 10°C; with aluminum chloride a temperature of 55–60°C is desirable.

Yields in the hydrogen fluoride and aluminum chloride processes are comparable (21). In each case an excess of benzene over olefin is charged. The yields and catalyst requirements depend a great deal on the olefin charged. The presence of olefins above dodecene leads to larger aluminum chloride consumption and lower alkylate yields (22).

In the alkylation of benzene with 1-dodecene, a straight-chain olefin, hydrogen fluoride gives a higher yield than either sulfuric acid or promoted aluminum chloride (23). The product may contain the phenyl group on any carbon from number 2 to number 6 of the dodecane chain, and aluminum chloride is capable of isomerizing these isomers to an equilibrium mixture. Alkylations with higher molecular weight olefins cannot be expected to give a simple product.

Substituted Benzenes. The ease of alkylation of a substituted aromatic hydrocarbon is dependent on the nature (activating influence) of the substituent. In the case of an alkylbenzene, such as toluene, the alkyl group increases the ease or rate of substitution; the alkyl group increases electron density in the ortho and para positions owing to some form of an electronic effect (12). In the alkylation of benzene, the insertion of the first alkyl group facilitates substitution of the second alkyl group, and yields of di- and trialkyl derivatives may be significant. In order to reduce the extent of polysubstitution, a large molar ratio (between 4:1 and 10:1) of benzene to olefin is often required in commercial plants preparing monoalkylbenzenes.

The entering alkyl group can be oriented in positions ortho, meta, or para to the directing group. With an alkylbenzene, the position taken is to a large extent a function of the activity of the attacking carbonium ion, and steric factors. The data which follow on the distribution of isomers, in percent, in the monoalkylation of toluene (11) show that a very reactive carbonium ion such as ethyl is not highly selective as to orientation, whereas a carbonium ion of low reactivity such as *t*-butyl is selective.

Entering group	Ortho	Meta	Para
methyl	53.8	17.3	28.8
ethyl	45	30	25
isopropyl	37.5	29.8	32.7
<i>t</i> -butyl	0	7	93

The extent of ortho substitution in comparison to para substitution is mainly controlled by steric conditions of both substituent and substituting groups.

The preceding information indicates that clean-cut alkylation to produce specific disubstituted compounds is seldom realized; furthermore, separation of the pure isomers from the reaction mixture is in most cases not readily accomplished. An exception is the preparation of diisopropylbenzene by an alkylation process using a silica–alumina catalyst. The alkylation can be conducted so as to give primarily the meta and para isomers (25,26), and these can be separated by fractionation (boiling points 203.18 and 201.37°C) (24).

The alkylation of xylenes with ethylene, propylene (27), and isobutylene (28) can be controlled in certain cases to give products of definite orientation.

Polycyclic Hydrocarbons. The alkylation of polycyclic hydrocarbons does not proceed in an orderly manner. The alkylation of naphthalene gives substitution in both 1- and 2-positions, with other side reactions (29,30). Amylnaphthalene is prepared from pentenes (that is, straight-chain C₅H₁₀) at 180°C using aluminum chloride promoted by amyl chloride as catalyst (31). The inferior yield of mono-alkyl derivatives is in part the result of formation of considerable amounts of poly-alkyl derivatives.

Dealkylation. The alkylation reaction as written is reversible and attempts have been made to determine the value of this equilibrium constant (32). At elevated temperatures the reverse reaction becomes appreciable. Tertiary alkyl groups are particularly susceptible to cleavage.

Dealkylation as a separate reaction in itself is not practiced commercially on a large scale. Transalkylation, a form of dealkylation, is carried out in alkylation plants where an active catalyst, such as aluminum chloride, is employed. For example, the polyethylbenzenes produced in the ethylation of benzene are dealkylated by transalkylation with benzene.

A hydrodealkylation process, trademark Hydeal, is carried out commercially in the demethylation of toluene and 1- or 2-methylnaphthalene to produce benzene and naphthalene (33).

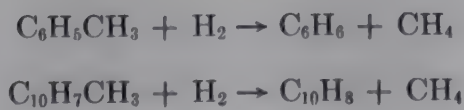


Table 1. U.S. Production of Four Alkylates

Product	Reactants	Reaction conditions					Trans-alkylation	Production
		Catalyst	Temperature, °C	Pressure, psi	Contact time, minutes	Molar ratio ^a		
isoparaffin alkylate	olefin (propylene, butenes) and isobutane	H ₂ SO ₄	0-10	135	5-40	8-14	0.3-2.0 lb/gal alkylate	296,750 bbl/day
		HF	0-40	135	5-25	8-14	0.2-0.8 lb/bbl alkylate	95,819 bbl/day
ethylbenzene	ethylene and benzene	AlCl ₃ -HCl	93	15		2.0	1-3 lb/100 lb ethylbenzene	1,661 × 10 ⁶ lb/yr ^{b,c}
		supported H ₃ PO ₄	200-250	500-900		5-10	50 gal ethylbenzene/lb catalyst	
		Alkar	150-250	400-700				
cumene	propylene and benzene	H ₂ SO ₄	35-40	165	35	6	10-12 vol cumene/vol H ₂ SO ₄	219 × 10 ⁶ lb/yr ^b
		supported H ₃ PO ₄	180	500		10	200 gal cumene/lb catalyst	
dodecylbenzene (detergent alkylate)	propylene trimer and benzene	HF	10			8		492 × 10 ⁶ lb/yr ^{b,d}
		AlCl ₃ -HCl	55-60				1-3 lb AlCl ₃ /150 lb alkylate	
		H ₂ SO ₄	10-20		60	3.5	0.87 lb alkylate/lb H ₂ SO ₄	

^a Molar ratio of isobutane or benzene to olefin.^b U.S. Tariff Commission Report, *Synthetic Organic Chemicals, U.S. Production and Sales, 1960*. TC Publication 34.^c Includes ethylbenzene by fractionation of C₈ aromatics.^d Includes keryl-type detergent alkylate.

The dealkylation can be conducted thermally or with advantage in the presence of a catalyst. A 10% MoO₃ on silica-stabilized, high-surface alumina (34) and a catalyst of cobalt molybdate on silica-stabilized alumina in the presence of steam (35) are reported as effective. The thermal reaction at either 500–600°C and 250 atmospheres of hydrogen or 700–950°C and atmospheric pressure has been shown to possess a rate dependency which is first order in respect to the hydrocarbon and one-half order in respect to hydrogen pressure (36, 37).

Table 1 summarizes some of the pertinent facts as to processes available for the manufacture of four alkylation products which are produced in large amounts. The values given represent typical data, but in some cases are rough estimates. Isoparaffin alkylate is the commodity in largest volume; 392,569 barrels per day is the capacity of all plants. Of this amount, 75% (269,750 barrels per day) represents product using sulfuric acid as catalyst. Of the two olefins used in isoparaffin alkylation, butylenes account for 80% of the alkylate. The alkylate blended into aviation gasolines consumes 40% of the total production.

An isoparaffin alkylation plant costs about \$10–\$15 per ton of alkylate per year. The remaining three products—ethylbenzene, cumene, and dodecylbenzene—require plants which cost in the range \$50–\$75 per ton per year. These figures depend not only on the size of the plant but also on the necessary auxiliary equipment.

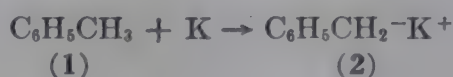
FREE-RADICAL ALKYLATION OF AROMATIC HYDROCARBONS

Aromatic hydrocarbons are susceptible to attack by free radicals, leading to substitution products (38,39). Thus, lead tetraacetate upon heating in acetic acid decomposes with formation of methyl radicals which attack benzene. The substitution does not follow the rules of the acid-catalyzed (electrophilic) process for either orientation or activation. This free-radical process has no commercial application at present.

CARBANION ALKYLATION OF AROMATIC HYDROCARBONS

Olefins can be brought into an alkylation reaction with aromatics in the presence of alkali metals or derivatives of alkali metals. Theoretically, with an alkylbenzene, two reactions can occur: alkylation of the aromatic ring, and alkylation of the side chain. In contrast to the acid-catalyzed reactions, alkylation occurs in the side chain with any alkylbenzene which has a benzylic hydrogen (hydrogen on an α carbon atom in a side chain). Ring alkylation can be obtained to a small extent, but side chain alkylation is preferred and proceeds more smoothly (40). Olefins which can be used include ethylene, propylene, styrene, and less successfully, the butylenes and higher olefins. Catalysts employed are sodium and potassium, their hydrides, benzylsodium, and reaction products of alkali metals with chlorotoluene or anthracene.

The reaction proceeds at temperatures of 100–200°C, depending on the catalyst system and the olefin. For example, the alkylation of toluene (1.0 mole) with propylene (0.485 mole) can be conducted with a potassium catalyst at a temperature of 149°C with a yield of about 75% based on propylene (41). The product is a mixture of isobutylbenzene and *n*-butylbenzene in ratios of 10 to 1. The reaction mechanism can be formulated as follows:



conditions is required. Olefins used are both butylene and propylene polymers to give the respective octyl-, nonyl-, and dodecylphenol with a branched-chain alkyl group. The alkylation can be catalyzed by a sulfonic acid resin at 70–110°C (45) or by *p*-toluenesulfonic acid hydrate ($\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}\cdot\text{H}_2\text{O}$) at 80–150°C (46) or by a Superfiltrol clay at 80°C (47).

Boron fluoride is an effective catalyst for this alkylation and is used commercially. The quality of product is dependent on the alkylation conditions. In the alkylation of phenol with diisobutylene, the optimum conditions for production of *p*-octylphenol have been stated as: (a) addition of boron fluoride to the phenol before addition of the olefin; (b) rapid addition of the olefin; (c) conducting the reaction for only a short time after olefin addition; (d) a reaction temperature not exceeding 70°C; (e) a catalyst concentration not greater than 0.5 wt % (48).

The alkylation of *p*-cresol with isobutylene yields 2,6-di-*t*-butyl-4-methylphenol, which is used as an antioxidant. Some of the operational details have been described for alkylation of a mixture of *m*- and *p*-cresol, each of which forms a dibutyl derivative (49,50). Sulfuric acid in amounts of 5 wt % of the cresol is a satisfactory catalyst at a temperature not greater than 100°C. The alkylation can be conducted with diluted gas stream, preferably added in vapor form, containing both isobutylene and butenes, although the latter do not react.

With thiophenol the olefin reaction with the usual acid catalysts gives not an alkylthiophenol but the alkyl phenyl sulfide (51). However, a procedure has been developed for alkylation in the ring using boron fluoride as catalyst to give exclusively para substitution (52).

Metal-Catalyzed Phenol Alkylation. The alkylation of phenols with olefins can be accomplished by the use of metal salts of the phenol. (See Alkylphenols.) Effective metals are those which form salts with the phenol (for example, zinc, aluminum, magnesium, calcium, etc) (53,54). The remarkable feature of this process is that ortho substitution is obtained almost exclusively; consequently, this process is used commercially to prepare ortho-substituted phenols. Not only phenol, but also *o*-cresol, *p*-cresol, and 2-naphthol can be alkylated with such olefins as ethylene, propylene, butylenes, and cyclohexene. The reaction is run at temperatures in the range 100–350°C, depending on the olefin, with a catalyst such as aluminum or zinc in amounts of 2 wt % of the phenol. The ease of alkylation depends on the olefin. The reaction proceeds with the greatest ease with isobutylene and with the least ease with ethylene (55). With aluminum phenolate, phenol can be butylated at low temperatures (105–115°C) with a product distribution, in percent yield, as follows:

phenol	5	2,6-di- <i>t</i> -butylphenol	36
2- <i>t</i> -butylphenol	46	2,4-di- <i>t</i> -butylphenol	5
4- <i>t</i> -butylphenol	1	2,4,6-tri- <i>t</i> -butylphenol	6

Alkylation of Aromatic Amines

Aromatic amines are not subject to facile alkylation in the ring by normal procedures with acid catalysts. The basic (electron-donating) amine group combines with the acid-type catalyst (electron-accepting) and decreases or nullifies activity. In isolated cases, alkylation can be carried out. Thus diphenylamine can be alkylated

at temperatures of 150–200°C with either styrene or diisobutylene in the presence of aluminum chloride to produce an alkylated amine (56).

The ring alkylation of primary and secondary aromatic amines can be carried out with a catalyst of the aluminum anilide type to give exclusively ortho substitution (57,58). Thus aniline can be alkylated to produce either 2-ethyl- or 2,6-diethyl-aniline using temperatures in the range 300–330°C. The more highly branched olefins, such as isobutylene, are less suitable than ethylene for this type of alkylation.

Nitrogen Alkylation

The placement of an alkyl group on the nitrogen atom of an amine can be achieved using numerous reagents and processes. The particular method chosen depends on the nature of the alkyl group to be inserted and the amine in question. Reference 59 gives a comprehensive summary of amine alkylation.

Alcohol Reagents. Alcohols react with ammonia or amines to give alkyl derivatives (see Ammonolysis). This method proceeds most readily with primary alcohols, less readily with secondary alcohols, and is impractical with tertiary alcohols. With ammonia, temperatures of about 400°C in the presence of a metal oxide as catalyst are required; a mixture of primary, secondary, and tertiary amines is obtained. Thus, the methanol–ammonia reaction is the basis for the manufacture of the methylamines (60). Likewise, such alcohols as ethyl and butyl can be used to give corresponding amines.

Aromatic amines can be alkylated by alcohols in the presence of an acid at temperatures of about 200°C. The reaction cannot be controlled to give solely the monoalkyl derivatives, but can be used for an efficient preparation of the *N,N*-dialkyl derivatives. *N,N*-Dimethylaniline and *N,N*-diethylaniline can be prepared from aniline and the corresponding alcohol with sulfuric acid as catalyst (61,62), or over an alumina catalyst at 300°C (63).

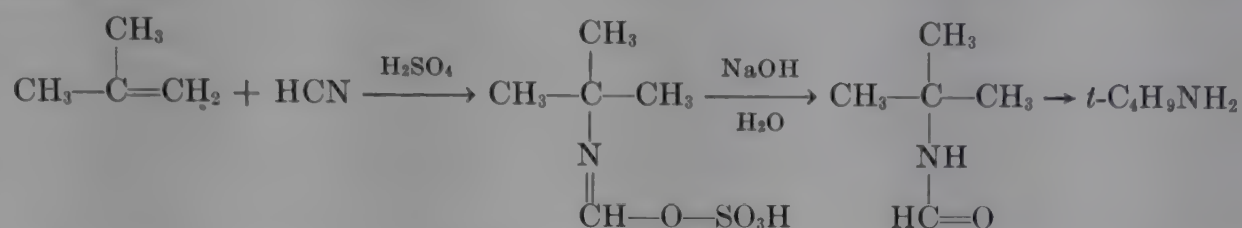
Alkyl Halide Reagents. The reaction of an alkyl halide with ammonia or an amine has long been used, particularly in the laboratory, to prepare alkylamines (59). Primary alkyl halides generally enter into the alkylation with little difficulty, the secondary alkyl halides not as readily, and the tertiary alkyl halides poorly. The reaction is often run in a mutual solvent, and provision must be made to neutralize the acid formed. This means of preparation leads to mixtures of primary, secondary, and tertiary amines, the relative proportions of which can be partly controlled by reaction conditions. The commercial preparation of amylamines from secondary amyl halides in an alcohol solution at about 165°C yields a product consisting of three parts of primary amine and two parts of secondary amine (64).

Olefin Reagents. Alkylamines can be prepared by the direct addition of an olefin to ammonia or an amine using alkali metals as catalysts. Ammonia and ethylene react at 175–200°C and 800–1000 atmospheres to give ethylamine (65). Higher olefins also react to give amines in moderate yields. These are formed according to Markownikoff's rule—that is, the —NH_2 attaches to that carbon atom which has the fewest hydrogens.

The ethylation of amines, such as dibutylamine, has been conducted with the sodium derivatives. When ethylene is reacted with $(\text{C}_4\text{H}_9)_2\text{NNa}$ (from Na and butadiene in $(\text{C}_4\text{H}_9)_2\text{NH}$) at 132–135°C, the ethyl derivative, $(\text{C}_4\text{H}_9)_2\text{NC}_2\text{H}_5$, is obtained in 63% yield (66).

A more clean-cut alkylation is obtained in the ethylation of arylamines. Aniline can be alkylated at 275°C in the presence of sodamide to give a 75% yield of *N*-ethylaniline with little diethylation (66). The reaction in the presence of small amounts of copper oxide gives an 86% yield of *N*-ethylaniline (58). The reaction does not proceed well with the higher olefins. The nitrogen alkylation obtained with an alkali metal catalyst is in contrast with the ring alkylation previously mentioned with aluminum anilide catalysts.

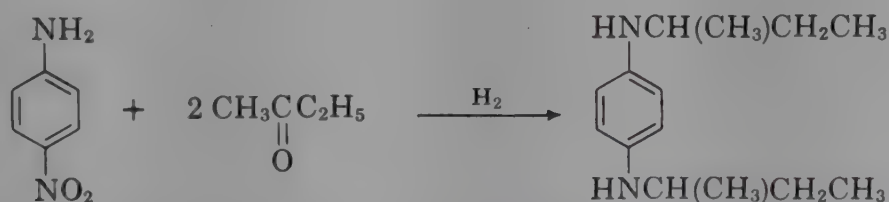
An indirect route to the preparation of alkylamines is the addition of hydrogen cyanide to an olefin followed by hydrolysis (Ritter reaction). The reaction works well with tertiary olefins to give a tertiary alkylamine, illustrated by the reaction with isobutylene (67).



By the use of butylene polymers or propylene polymers, *t*-alkylamines with C₈, C₉, and higher groups are manufactured commercially (see Amines).

Carbonyl Reagents. The reaction of either ammonia or an amine and a carbonyl compound in the presence of a proper hydrogenation catalyst and hydrogen can be controlled in many cases to give high yields of an alkyl derivative. This process, called *reductive alkylation*, has been adopted for commercial use; it is based mainly on ketones, although aldehydes can be used with suitable control (68).

The reductive alkylation of *p*-phenylenediamine or *p*-nitroaniline with methyl ethyl ketone gives *N,N'*-di-*sec*-butyl-*p*-phenylenediamine, which is useful as an antioxidant.



A number of catalysts have been reported as suitable including copper chromite (69), molybdenum sulfide, Raney nickel, platinum black, supported platinum, and palladium (59), at temperatures in the range of 125–200°C and hydrogen pressures of 500–1500 psi. A similar reaction can be used with higher-weight carbonyls to prepare larger alkyl-substituted derivatives, some of which are useful as rubber additives.

Quaternary Ammonium Compounds. The further alkylation of a tertiary amine leads to formation of quaternary ammonium compounds (qv). The common method of preparation is the reaction of an active alkyl halide with a tertiary amine at temperatures of 100–150°C. The product is an ammonium halide which can be transformed to the hydroxide by passage over an anion exchange resin.

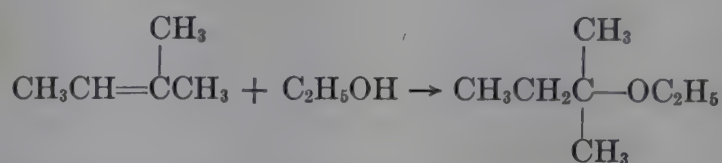
Oxygen and Sulfur Alkylation

Alkyl Halide Reagents. Ethers are produced by the reaction of an alkyl halide with an alkali metal salt of either an alcohol or phenol. The reaction proceeds cleanly with active primary halides such as benzyl chloride. The reaction mechanism is

described as an example of bimolecular nucleophilic substitution (S_N2 , where S stands for substitution, N for nucleophilic, and 2 for bimolecular) (12) and certain cases have been studied in detail (70). Secondary alkyl halide reactions also involve a unimolecular nucleophilic substitution, and variation in reaction conditions may have different effects with the primary and secondary halides. Tertiary alkyl halides are subject to an elimination reaction in the presence of a basic anion and are not suitable for preparation of tertiary alkyl ethers. The alkyl chlorides are less reactive chemically than the bromides or iodides, but economic factors necessitate use of the chlorides for large-scale operation.

Ethers of cellulose are prepared by an alkylation of alkali cellulose with an alkyl halide such as benzyl chloride, ethyl chloride, and methyl chloride (see Cellulose derivatives).

Olefin Reagents. The addition of an alcohol or phenol to an olefin can be used to produce secondary or tertiary alkyl ethers. For example, ethyl alcohol adds to 2-methyl-2-butene at 60°C in the presence of small amounts of sulfuric acid to yield *t*-amyl ethyl ether (71):



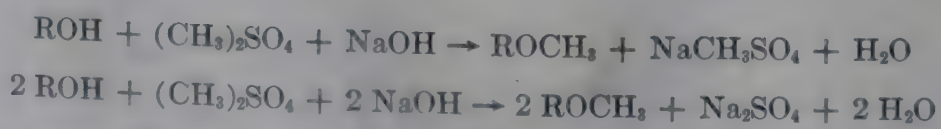
A similar reaction occurs when the olefin is replaced by a tertiary alcohol which readily dehydrates to the olefin. Either diluted sulfuric acid or aqueous sodium acid sulfate is able to condense *t*-butyl alcohol with ethyl or isopropyl alcohol (72).

In order to form a tertiary alkyl ether of a phenol, an acid catalyst must be used in small amounts to avoid ring alkylation (73). The preparation of butyl ethers of various phenols with yields of about 60% can be conducted at temperatures in the range -10 to 25°C with sulfuric acid in amounts of 0.5 wt %.

The alkylation of thiophenols with olefins gives thioethers (51). The position of the substituent on the olefin is according to Markownikoff's rule. Ring alkylation is not observed unless boron trifluoride is used (52).

The alkylation of mercaptans with olefins can also be carried out using metals in Groups I, II, and III of the Periodic Table (74). The addition can be controlled either to follow or deviate from Markownikoff's rule; thiophenol adds to propylene (200°C, 40 atmospheres pressure) with an aluminum catalyst to give a 77% yield of isopropyl phenyl sulfide, but with a sodium catalyst (250°C, 50 atmospheres pressure) gives a 72% yield of *n*-propyl phenyl sulfide.

Alkyl Sulfate Reagent. Dimethyl sulfate and diethyl sulfate are two common alkylating reagents for the preparation of ethers from both alcohols and phenols. The reaction is run in the presence of a base, generally a metal hydroxide. One equivalent of alkylation is generally realized per mole of sulfate, but in some cases both alkyl groups can be forced to react by the use of concentrated solutions and a higher temperature (75).



A polar solvent, such as water, is generally used, but solvents such as xylene with sodium carbonate can be used with advantage in certain alkylations (76).

Dehydration. The dehydration of alcohols, or of an alcohol and phenol, produces ethers. This reaction can be catalyzed either by acid-type catalysts or by metal oxides at elevated temperature. Diethyl ether is produced as a by-product in the hydration of ethylene to ethyl alcohol as a result of the following equilibrium:



Sulfuric acid is an effective catalyst in this equilibrium, both for ethanol and for 2-propanol (77).

The passage of methanol and ethanol over alumina catalysts at temperatures of 200–300°C can be regulated to give a high yield of the corresponding ether. Likewise, the dehydration of a phenol-methyl alcohol mixture at 200°C over alumina produces methyl phenyl ether (anisole) (78, 79). Higher temperatures (near 300°C) give rise to ring methylation.

Organometallics

The organometallic manufactured in largest quantity is tetraethyllead. The original Kraus-Collis process with improvements is in use and consists of the reaction of monosodium-lead alloy with ethyl chloride.



The sodium-lead alloy and ethyl chloride are brought into reaction in an autoclave at temperatures of 80–120°C and pressures of 100–225 psi. The tetraethyllead is steam-distilled from the sodium chloride and lead, and purified. The yields are on the average of 90% based on sodium and 22% based on the lead charged (80).

The preparation of tetramethyllead is carried out in a similar manner (80). A catalyst such as aluminum chloride is needed for the methyl chloride-sodium alloy reaction, which is carried out at temperatures of 90–100°C with yields of 85%.

Alkylaluminum derivatives have become an item of importance since about 1953 at which time Ziegler reported their catalytic activity for polymerization, and means for their preparation (81). (See Aluminum compounds.) The method of preparation depends on the particular alkyl derivative, but involves one of the three following alkylation reactions (82): (a) reaction of an alkyl halide with an aluminum-magnesium alloy; (b) addition of an olefin to aluminum hydride; and (c) reaction of aluminum, hydrogen, and an olefin.

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ALKYLPHENOLS

This article discusses those alkylphenols that are manufactured by alkylation of phenol or its homologs. Cresols and xylenols, which are obtained from coal tar, are discussed separately. (See Cresols.) This article also discusses certain alkylphenols, cardanol and hydrocardanol, that are derived from natural sources, and such related products as *o*- and *p*-phenylphenols.

General Properties

Substitution into the nucleus of a phenol molecule by one or more alkyl groups markedly affects the properties of the phenol. Thus, alkyl groups attached to carbon atoms ortho or para to the hydroxyl group generally prevent further reaction at these positions. The effect is most marked in subsequent condensations with such compounds as formaldehyde. A phenol with only one available ortho or para position reacts with formaldehyde to give only a dimeric product, a substituted diphenylmethane. (See p. 903.) Polymeric products, on the other hand, are obtained when two of these positions are unsubstituted; and when all three are available the polymeric products are, in addition, crosslinked. (See Phenoplasts.)

Alkyl groups generally reduce the influence of the hydroxyl group and thus detract from the phenolic function of the molecule. The solubility in water and the density of the substituted phenol decrease with the size of the alkyl group and the solubility in hydrocarbon solvents increases. The most noticeable effect of an alkyl substituent is, however, on the caustic solubility of the phenol. Phenols substituted in the para posi-

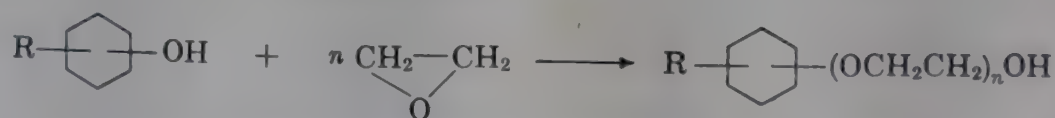
tion with such large alkyl groups as 1,1,3,3-tetramethylbutyl are relatively insoluble in cold dilute aqueous alkali but are converted to insoluble sodium salts on treatment with warm solutions of caustic soda in concentrations of about 10% and higher. When a large alkyl group is ortho to the hydroxyl, the phenol is insoluble in strong and even hot aqueous caustic soda. Such phenols are generally referred to as "crypto" phenols. Cryptophenols are, however, soluble in Claisen solution (350 g of potassium hydroxide in 250 g of water, made up to 1 liter with methanol), in which respect they differ from phenols having two bulky alkyl groups—for example, a *tert*-butyl group in each position ortho to the hydroxyl. In these, known as "hindered" phenols (1), the normal reactivity of the hydroxyl group is virtually lost. In addition to being completely insoluble in aqueous and alcoholic alkali, they cannot be converted to such derivatives as esters by the normal techniques, and sometimes not at all, nor do they give the customary phenol coloration with aqueous or alcoholic ferric chloride.

Alkylphenols are, in general, reactive compounds and behave very much like phenol itself except when the position and nature of the alkyl groups preclude it. The following reactions are of prime importance commercially.

Ether Formation. Like that of phenol itself, the hydroxyl group of an alkylphenol can be converted to an ether group by reacting with an alkyl halide, sulfate, etc, in presence of alkali, or with an olefin, particularly a primary or secondary olefin, in presence of an acid catalyst. Tertiary olefins, because of their greater tendency to enter the phenol nucleus, give ethers only under the most mild reaction conditions.

The methyl ether of 3-methyl-6-*tert*-butylphenol is used as an intermediate in the manufacture of musk ambrette (2,4-dinitro-3-methyl-6-*tert*-butylanisole), but otherwise ethers of alkyl-substituted monohydric phenols have little or no commercial application. Alkylphenoxyacetic acids, which are in fact substituted ethers of alkylphenols, are, however, frequently used for the identification of alkylphenols; they are normally highly crystalline compounds readily prepared by reacting the alkylphenol with chloroacetic acid in presence of excess caustic soda.

Phenols are readily condensed with ethylene oxide using a basic catalyst to effect polyoxyethylation of the hydroxyl group:



The products are actually mixtures of varying chain length, n representing an average value. Because of the hydrophobic and hydrophilic nature of the alkylphenyl group and the polyoxyethylene chain, respectively, these condensates are extremely active surface-active agents. (See Surfactants.) Being nonionic, they cannot form salts with metal ions and are consequently equally effective in hard and soft water. The solubility characteristics of these materials are dependent on both the length of the alkyl chain and the number of ethylene oxide molecules condensed; with *p*-alkylphenols, complete water miscibility is usually achieved when n is equal to or greater than the number of carbon atoms in the alkyl group. The water-soluble condensates, particularly from *p*-alkylphenols such as 1,1,3,3-tetramethylbutyl, nonyl, and dodecyl, are used in very large quantities as detergents, wetting agents, and emulsifiers for aromatic solvents. The water-insoluble condensates are readily converted to water-soluble alkyl metal or amine sulfates such as



where $X = \text{Na}$, $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$, etc. These are valuable anionic detergents and wetting agents and are used to increase foam production in domestic detergents.

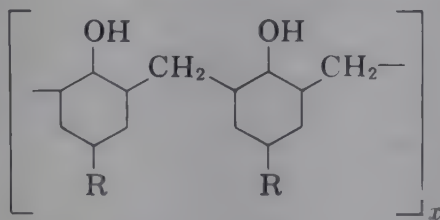
Nitration. Little difficulty is normally encountered in nitrating alkylphenols if reaction conditions are carefully controlled; as would be expected, the nitro groups enter the nucleus in free positions ortho and/or para to the phenolic hydroxyl. In 2,4,6-trialkylphenols—for example, 4-methyl-2,6-di-*tert*-butylphenol—nitration can occur meta to the hydroxyl group. More vigorous conditions may cause destructive oxidation of the phenol, or replacement of *tert*-butyl groups ortho or para to the hydroxyl by nitro groups. For example, nitration of 3-methyl-6-*tert*-butylphenol in acetic acid at -10°C affords a mixture of the 2- and 4-nitro derivatives, whereas at higher temperatures in ether solution with excess nitric acid the product is largely 2,4,6-trinitro-*m*-cresol. Substantial quantities of 4,6-dinitro-2-*sec*-butylphenol are manufactured for use as a general herbicide; it is usually applied by spraying as an aqueous solution of an amine salt. It is claimed to be less toxic than 4,6-dinitro-*o*-cresol (DNOC).

Sulfurization. Alkylphenols react readily with the mono- and dichlorides of sulfur. Under controlled conditions the products are respectively bisphenol disulfides (1) and bisphenol monosulfides (2); more extreme conditions or further reaction with sulfur or phosphorus pentasulfide afford complex polysulfides.



The bisphenol monosulfides are the most important commercially. From *p*-alkylphenols, such as *p*-*tert*-octylphenol (*p*-(1,1,3,3-tetramethylbutyl)phenol) or *p*-nonylphenol (see p. 908), the monosulfides are widely used, in the form of their metal salts, particularly calcium, barium, or zinc, as lubricating oil detergents. Other bisphenol monosulfides are valuable antioxidants in rubber and polyolefins. The most important is probably that based on 3-methyl-6-*tert*-butylphenol (see 4,4'-thiobis(3-methyl-6-*tert*-butylphenol), p. 914).

Condensation with Aldehydes and Ketones. Aldehydes readily condense with phenols unsubstituted in positions ortho and/or para to the hydroxyl groups to yield polymers or diphenylmethanes, depending on the nature of the phenol used. Phenol itself, which has three positions available for substitution, affords on reaction with formaldehyde the well-known phenol-formaldehyde resins developed at the beginning of the century by Baekeland. *p*-Alkyl-substituted phenols similarly yield polymers



but these polymers, unlike those from ordinary phenol, are oil-soluble. The condensation reaction can be carried out in the presence of an acid (such as hydrochloric or oxalic) or a base (such as sodium hydroxide, sodium carbonate, lime, or an amine).

Such polymers and particularly those from such alkylphenols as *p*-*tert*-butyl-, *p*-*tert*-amyl-, and *p*-(1,1,3,3-tetramethylbutyl)-, which are available commercially in high purity, are now widely used in varnish manufacture. For this purpose they are compounded with a drying oil; tung oil (China wood oil) probably gives the best results. The varnishes give films which have excellent color stability, durability, and resistance, particularly to water and alkali.

Nonresinous condensates of alkylphenols and aldehydes may also be prepared. A wide variety of these products, which are substituted diphenylmethane derivatives, are manufactured for use as antioxidants, particularly in rubber, olefin polymers, and lubricating oils.

Substituted diphenylmethanes are also obtained by condensation of a phenol and a ketone. The most important commercially is "bisphenol A" (see p. 912), from phenol and acetone, but alkylphenol-acetone condensates are also available.

Manufacture

The alkylphenols are generally manufactured by addition of an alkyl group to a simpler phenol. (See Alkylation.) The source of the alkyl group may be an aliphatic alcohol, a chloride, or an olefin. Olefins are preferred commercially; they are easily handled and readily available at low cost. The alkylation reaction is usually carried out at atmospheric pressure in presence of an acid or Lewis acid catalyst such as phosphoric, hydrochloric, or sulfuric acid, ferric or aluminum chloride, or boron trifluoride. In practice sulfuric acid, boron trifluoride, and aluminum chloride are commonly used.

In the presence of acid catalysts substitution in phenol normally occurs at the ortho and para positions relative to the hydroxyl group. All such positions are substituted to a greater or lesser extent depending on the reaction conditions—in particular, reaction temperature, nature of catalyst and catalyst concentration, and structure of the olefin employed. When phenol containing 5% sulfuric acid is alkylated with 1 molar equivalent of isobutylene (2-methylpropene) at 70°C, and subsequently heated at 150°C for 1 hour, the approximate composition of the product, in weight percent, changes as shown below:

	<i>Phenol</i>	<i>2-tert-Butylphenol</i>	<i>4-tert-Butylphenol</i>	<i>2,4-Di-tert-butylphenol</i>
composition at 70°C	19	15	26	39
composition at 150°C	7	15	63	14

At still higher temperatures dealkylation and, to a lesser extent, isomerization to the relatively stable 3-*tert*-butylphenol occur.

The nature of the products obtained on alkylation of cresols and xylenols is dependent also to a large extent on the positions already occupied by the methyl groups. The pattern of substitution has been examined in greatest detail with isobutylene and diisobutylene (2,4,4-trimethyl-1-pentene and -2-pentene) as alkylating agents. The following conclusions can be drawn:

1. The *tert*-butyl group (from isobutylene) cannot enter the nucleus at the carbon atom between meta positions already substituted by methyl groups or by a methyl and a hydroxyl group. Thus *m*-cresol (3-methylphenol) does not yield a derivative containing a *tert*-butyl group in the 2 position and 3,5-dimethylphenol is incapable of being alkylated in the nucleus with isobutylene.

2. The 1,1,3,3-tetramethylbutyl group, $-\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{CH}_3)_3$, from diisobutylene, will not enter any position which cannot be substituted by a *tert*-butyl group nor, in addition, at any carbon atom adjacent to a carbon atom already attached to a methyl group. Hence no derivative of 2,5-dimethylphenol substituted in the nucleus with the tetramethylbutyl group is known.

In practice the ease with which alkylphenols, particularly *tert*-alkylphenols, rearrange and dealkylate in presence of an acid catalyst is of considerable value. High yields of any desired compound can be achieved by separating the by-products—for example, by distillation—and returning them to the alkylation stage of the process. The reversibility of the alkylation reaction affords a means of separating certain phenols, such as *m*- and *p*-cresol, which are available from natural sources but are not easily separated from one another by normal physical techniques. The di-*tert*-butyl derivatives of these cresols are readily separable by distillation and may then, individually, be dealkylated to the pure isomers. Likewise mixtures of 2,4- and 2,5-dimethylphenols may be separated into the single isomers via their *tert*-butyl derivatives.

Recently (2) alkylation of a phenol with an olefin in presence of an aluminum phenolate catalyst has attracted considerable attention. (See Alkylation.) Unlike those obtained by acid-catalyzed reaction, the products are predominantly ortho substituted. From phenol and isobutylene, for example, high yields of the hitherto relatively inaccessible 2-*tert*-butyl- and 2,6-di-*tert*-butylphenol can be obtained. Such ortho-substituted phenols are now commercially available in tonnage quantities and are widely used as antioxidants themselves and as intermediates in the manufacture of more complex antioxidants.

Analysis

Many of the common analytical methods for phenol are directly applicable to those alkylphenols containing either a free ortho or a free para position. Thus, for example, various colorimetric procedures have been developed using such reagents as diazotized sulfanilic acid, 4-aminoantipyrine, 2,6-dibromo-*N*-chloro-*p*-benzoquinone imine, and Millon reagent. When the ortho and para positions are substituted, recourse is often made to oxidation either with phosphotungstic-phosphomolybdic acid reagent, the blue tungstic oxide produced being measured, or with ferric ion, the resulting ferrous iron being determined with 2,2'-dipyridine or bathophenanthroline (4,7-diphenyl-1,10-phenanthroline).

Liquid-phase partition chromatography has been used for some time for the separation of phenol, cresol, and xlenol mixtures, the subsequent determination of individual components being carried out by ultraviolet spectroscopy (3). Extensions of this method have, on occasion, been found useful for the analysis of mixtures of the higher alkylphenols (butyl-, octyl-, and phenylphenols). The potentialities of gas-liquid chromatography are currently attracting attention, particularly since many of the difficulties of dealing with such high-boiling compounds have been overcome.

All alkylphenols absorb strongly in the ultraviolet spectral region and spectroscopic techniques have been widely used for their determination in nonabsorbing media. Interference from other ultraviolet absorbing materials may often be overcome by utilizing the bathochromic shift (movement of the absorption maximum to a longer wavelength) which occurs on the addition of alkali (4).

Infrared spectroscopy is particularly useful for the identification of individual alkylphenols, the different arrangement and nature of the substituents producing characteristic absorption bands in the 8–15 micron region (5). Mixtures of alkylphenols can be quantitatively analyzed in those cases where individual sharp absorption bands are available for each component.

Alkylphenols are frequently characterized by the *hydroxyl value* (or *hydroxyl number*). This value, determined by esterification with acetic anhydride, is defined as the number of milligrams of potassium hydroxide equivalent to the amount of acid taken up on esterification of 1 gram of the alkylphenol. The hydroxyl value of pure phenol is 596; for alkylphenols it is, of course, correspondingly lower. Quantitative esterification of phenols with bulky alkyl groups ortho to the hydroxyl group, is, however, difficult to achieve in practice and, accordingly, reported values may not correspond to those calculated from the chemical formulas.

Individual Alkylphenols

***o*-tert-Butylphenol** ($(\text{CH}_3)_3\text{CC}_6\text{H}_4\text{OH}$), formula weight 150.2, is a pale yellow liquid. The commercial product has the following specifications: bp 224°C; freezing point -7°C ; flash point (open cup) 110°C; density 0.982²⁰. It is soluble in isopentane, toluene, ethyl alcohol, and 10% aqueous sodium hydroxide, but is insoluble in water. Applications are suggested as a chemical intermediate for synthetic resins, perfumes, surface-active agents, and plasticizers (6).

***m*-tert-Butylphenol** ($(\text{CH}_3)_3\text{CC}_6\text{H}_4\text{OH}$), formula weight 150.2, is available as a crystalline solid or as a eutectic mixture of meta and para isomers. The method of preparation has not yet been disclosed. The crystalline product is described as having greater than 95% purity, mp $>40^\circ\text{C}$, bp 237°C, specific gravity 0.963⁴⁵, and refractive index 1.5137 at 45°C. The eutectic mixture comprises 65% *m*- and 27% *p*-tert-butylphenol (remainder being other alkylphenols), mp approximately 15°C, bp 234–241°C, specific gravity 0.975²⁰, and refractive index 1.5232 at 18°C. *m*-tert-Butylphenol is insoluble in water, but is soluble in acetone, alcohols, and the common aromatic solvents. Its use has been suggested for preventing oxidation in rubber, oils, and resins, and also as an antiskinning agent. It is available in pilot-plant quantities (7).

***p*-tert-Butylphenol** ($(\text{CH}_3)_3\text{CC}_6\text{H}_4\text{OH}$), formula weight 150.2, has achieved considerable commercial importance in the manufacture of phenolic coating materials. U.S. production amounts to some thousands of tons yearly at a price of about 26¢ per lb. A typical specification for 98–99% material (the remainder is *o*-butyl and dibutyl by-products) is: mp 97–98°C; bp 239°C; specific gravity 0.905¹²⁰₄ (molten), 1.04²⁵₂₅ (crystals); and flash point (Pensky-Martens, closed cup) 235°F. It is available in polyethylene-lined paper sacks and fiber drums, and can be supplied molten in tank cars.

p-tert-Butylphenol is practically insoluble in hot and cold water, but quite soluble in aqueous alcoholic alkali and in hot aqueous alkali solutions. It dissolves readily in most oxygenated and chlorinated organic solvents, and in aromatic hydrocarbons; it is less soluble in aliphatic hydrocarbons. Reactions of *p*-tert-butylphenol are typical of its class. Most important is the condensation with formaldehyde, in the presence of either basic or acidic catalysts, to give light-colored, oil-soluble resins characterized by good resistance to acid, alkali, water, and light. These may be used to make dur-

able varnishes either directly by heating with a drying oil, or after first modifying by esterification with rosin or a fatty acid and then reacting with the drying oil. *p*-*tert*-Butylphenol resins are also important in formulating adhesives. Condensation of *p*-*tert*-butylphenol with acetylene gives a polymeric product with application as a tackifier for rubber and other elastomers. *p*-*tert*-Butylphenol itself is of value as a rubber anticracking agent and as a stabilizer in soap. Hydrogenation gives *cis*- and *trans*-4-*tert*-butylcyclohexanol, the acetates of which are used in perfumery as a substitute for lemongrass oil (8–11).

***p*-*tert*-Amylphenol** ($\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{C}_6\text{H}_4\text{OH}$), formula weight 164.2, is a white crystalline solid; mp 95°C, and bp 265–267°C. Grades of the commercial product can vary in color from pure white to dark cream with melting points between 81 and 91°C. It is practically insoluble in water but is soluble in 10% aqueous alkali, acetone, methanol, ether, and also in aromatic solvents. Like other para-substituted phenols, *p*-*tert*-amylphenol can be condensed with formaldehyde to form thermosetting or thermostable resins which are soluble in benzene, toluene, and drying oils; these resins are of value in varnish and paint manufacture. Another major use of *p*-*tert*-amylphenol is in the production of surface-active agents by reaction with ethylene oxide. These are of value as emulsifying and dispersing agents. Solutions of *p*-*tert*-amylphenol in alcohol/water are used in the manufacture of germicides, insecticides, and fumigants. *p*-*tert*-Amylphenol is also used as an intermediate in the manufacture of rubber chemicals and petroleum additives. *p*-*tert*-Amylphenol is available as a flaked solid in fiber drums or in sacks at about 25¢ per lb (10,12).

Heptylphenol, empirical formula $\text{C}_{13}\text{H}_{20}\text{O}$, is a viscous clear to pale yellow liquid with a mildly phenolic odor, made by alkylation of phenol with commercially available heptylenes. It is predominantly para-substituted, but consists of a mixture of isomers having structurally different alkyl groups. Heptylphenol, in keeping with the other alkylphenols, such as nonyl- and dodecyl-, is practically insoluble in hot or cold water. It is miscible with the common organic solvents, except for the lower aliphatic hydrocarbons, in which it is only partially soluble. Typical properties are: colorless to pale yellow viscous liquid; distillation range at 760 mm (Hg 5–95%) 277–305°C; viscosity at 20°C 2400 centistokes; flash point (Pensky-Martens, closed cup) 141°C; hydroxyl value 290. Being closely related chemically to octylphenol and nonylphenol, heptylphenol gives rise to intermediates in the manufacture of detergent-dispersant additives and lubricating oil additives. It may also be an intermediate in the production of plasticizers, stabilizers, and rubber chemicals (9).

***p*-*tert*-Octylphenol** (*p*-(1,1,3,3-tetramethylbutyl)phenol, diisobutylphenol, $(\text{CH}_3)_3\text{CCH}_2\text{C}(\text{CH}_3)_2\text{C}_6\text{H}_4\text{OH}$), formula weight 206.3, is made on a large scale and is usually supplied as a white flaked solid, although it can be supplied molten in tank cars. The U.S. price is in the range 21.5–23¢ per lb. The appearance of the flakes slowly changes on storage; they become more compact and, by sublimation, become covered with fine feathery crystals. This, of course, does not affect the quality of the product. A typical specification for a commercial product with a narrow distillation range is: *p*-*tert*-octylphenol content 98%; congealing point 81–83°C; bp (5–95%) 286–288°C; specific gravity 0.922₄²⁰; flash point (closed cup) 280°F; hydroxyl number 270; and color (40% in methanol) 10–20 APHA. Broader cut material (95% *p*-*tert*-octylphenol) might have a bp (5–95%) 280–290°C; congealing point 75–78°C. *p*-*tert*-Octylphenol is practically insoluble in hot and cold water and also in dilute alkalies, but is completely soluble in aqueous methanolic potassium hydroxide (Claisen alkali). It

is readily soluble in most organic solvents but only to a limited extent in aliphatic hydrocarbons. The main commercial uses of *p-tert*-octylphenol are in the manufacture of oil-soluble phenolic resins by condensation with formaldehyde and in the manufacture of nonionic wetting and dispersing agents by condensation with ethylene oxide. The calcium or barium salts of sulfides or formaldehyde condensates of *p-tert*-octylphenol are widely used as oil additives. *p-tert*-Octylphenol is a stabilizer for ethyl cellulose, improving its heat and ultraviolet stability. It is also used in the manufacture of dyestuffs, insecticides, bactericides, and pharmaceutical compounds. It also has bactericidal properties of its own, but is only active against Gram-positive bacteria, and has little or no effect on Gram-negative bacteria (9,13).

Nonylphenol, empirical formula $C_{15}H_{24}O$, is manufactured industrially by alkylation of phenol with mixed isomeric nonylenes (propylene trimer) in the presence of an acid catalyst, in either batchwise or continuous processes. In the reaction product, the para-substituted derivative predominates, with smaller amounts of the *o*- and 2,4-dinonylphenols also present. Separation of the *p*-nonylphenol, the desired product, is effected by the distillation of the crude reaction products under reduced pressure.

Production in the U.S. in 1960 was greater than 20,000 short tons. The price is 20¢ per lb in tanks and about 23¢ per lb in drums. Storage of the refined material, as with other alkylphenols, at elevated temperatures in the presence of air (oxygen), leads to color formation resulting in a yellow to brown product. Inert gas blankets, such as nitrogen, are frequently used in conjunction with stainless steel or specially treated storage tanks to maintain color stability.

A typical analysis of the commercially available nonylphenol is: color colorless to light yellow; boiling range, initial boiling point 287°C , 5% 292°C , 95% 301°C , final bp 306°C ; flash point (Tag open cup) 286°F ; specific gravity 0.945^{20}_{20} ; refractive index 1.512^{20}_{D} ; and hydroxyl number 253. The kinematic viscosity is approximately 300 centistokes at 100°F .

Nonylphenol is barely soluble in hot or cold water and aqueous alkali solutions in which soaplike phenolates of limited solubility are formed. It is soluble in Claisen solution and the common organic solvents acetone, benzene, carbon tetrachloride, ethyl alcohol, diethyl ether, and, to a limited extent, in the lower aliphatic hydrocarbons. Nonylphenol undergoes the normal reactions of the phenolic hydroxyl group as well as substitution in the benzene ring. By far the most important industrial reaction is etherification, whereby condensation with ethylene oxide using a basic catalyst gives the nonionic surface-active agent of the nonylphenoxypolyethoxyethanol type. Production of this condensate in the U.S. in 1960 reached 40,000 short tons, at a value of about 22¢ per lb. These ethers have good chemical stability and excellent wetting, emulsifying, and detergent properties. A major field of application is the textile industry, but use in the home is growing rapidly.

Nonylphenol reacts with aldehydes to yield phenolic resins. When used with other phenols, even in small quantities, it makes phenolic resins more water resistant, more soluble in oil, and improves electrical properties (13). In rubber chemistry, nonylphenol sulfide has been used as a reclaiming agent for synthetic rubber, and tris-*p*-nonylphenyl phosphite has been employed as a nonstaining rubber antioxidant. A variety of *p*-nonylphenyl derivatives have uses as polyvinyl chloride plasticizer intermediates (14). Among these are *p*-nonylphenyl benzoate, *p*-nonylphenyl alkane sulfonates, and *p*-nonylcyclohexanol. Other suggested fields of application for nonylphenol are in pharmaceuticals, corrosion inhibitors (15), dyestuffs, ore flotation agents (16), insecticides, bactericides, chemical stabilizers, and the leather industry.

Dodecylphenol, empirical formula $C_{18}H_{30}O$, is made from phenol and propylene tetramer and consists predominantly of a mixture of *p*-alkylphenols derived from various isomeric branched-chain dodecylenes. It is a multithousand-ton-per-year product which is priced at 20¢ per lb in tanks and about 23¢ per lb in drums. Dodecylphenol is similar to nonylphenol in solubility, being practically insoluble in hot or cold water and forming only partially water-soluble phenolates in aqueous alkalis. It is soluble in Claisen solution and the common organic solvents with the exception of the aliphatic hydrocarbons. Typical properties are: appearance colorless to pale yellow; boiling range (5–95%) 322–335°C; flash point (Pensky-Martens, closed cup) 141°C; specific gravity 0.940^{15,5}; hydroxyl number 214; and viscosity at 20°C 4660 centistokes.

Dodecylphenol undergoes the typical reactions of *p*-alkylphenols giving ethers, esters, sulfonic acids, halo and nitro derivatives as well as condensation and hydrogenation products. The alkali metal salts of its sulfonic acids have useful surface-active properties.

As with nonylphenol, dodecylphenol reacts with alkylene oxides, most usually ethylene oxide, to give long-chain polyethers which find wide applications as household and industrial nonionic detergents, and as wetting and emulsifying agents. Anionic surfactants, which are prepared by the sulfation of condensates containing about four to seven molecules of ethylene oxide per molecule of alkylphenol, are used in light-duty liquid detergents (13).

2,6-Di-*tert*-butylphenol $((CH_3)_3C(CH_3)_3CC_6H_3OH)$, has a formula weight of 206.3; mp 37°C; bp 253°C; flash point (open cup) 118°C; and density 0.914²⁰. It is made by reaction of phenol with isobutylene using aluminum phenolate as catalyst and is suggested as an intermediate for making synthetic resins, plasticizers, and surface-active agents. It is used as an antioxidant to inhibit gum formation in leaded gasoline, and its condensation product with formaldehyde is a particularly useful antioxidant for polymers, oils, and waxes (6).

3-Methyl-6-*tert*-butylphenol (mono-*tert*-butyl-*m*-cresol $((CH_3)_3C)(CH_3)C_6H_2OH$), formula weight 164.2, is a colorless to pale yellow crystalline solid; mp about 23°C; and bp 244°C. The commercial grade has the following specification: mp 21°C; bp 240–245°C; flash point (Pensky-Martens, closed cup) 220°F; vapor pressure (at 100°C) 5 mm Hg; and density 0.962³⁵ (9). It is available in drums and tank cars at about 55¢ per lb. 3-Methyl-6-*tert*-butylphenol is soluble in many common organic solvents, but practically insoluble in water and in cold dilute alkali. The compound itself differs from most alkylated phenols in that it combines with water to form a crystalline hydrate: $C_{11}H_{16}O \cdot \frac{1}{4}H_2O$, mp 37°C. Otherwise it undergoes most of the reactions typical of the lower alkylated phenols to form ethers, esters, alkyl, aryl, and halogen derivatives, as well as condensation and hydrogenation products. It is an effective antioxidant and stabilizer for coumarone-indene resins, polyvinyl ethers, and halogenated hydrocarbons such as trichloroethylene and perchloroethylene, and is an intermediate in the manufacture of antioxidants for rubber and also for other high polymers.

3-Methyl-6-*tert*-butylphenol is of particular value as an intermediate in the manufacture of musk ambrette (2,4-dinitro-3-methyl-6-*tert*-butylanisole), which is widely used as a fixative in the perfume industry (17,18). Further applications include its use as a germicide in disinfectant and antiseptic formulations, including anthelmintic and internal disinfectants, where its effectiveness is similar to that of thymol (3-methyl-6-isopropylphenol) (19).

3-Methyl-4,6-di-*tert*-butylphenol (4,6-di-*tert*-butyl-*m*-cresol, $((\text{CH}_3)_3\text{C})_2(\text{CH}_3)\text{-C}_6\text{H}_2\text{OH}$), formula weight 220.34, is a pale yellow crystalline solid: mp 61.2°C; bp 282°C. The commercial product has the following specification: mp 56.0°C; bp 285°C; d_4^{70} 0.915; flash point (Pensky-Martens, closed cup) >290°F; vapor pressure (at 135°C) 5 mm Hg (9). It is available in nonreturnable mild-steel drums. 3-Methyl-4,6-di-*tert*-butylphenol is practically insoluble in water and in aqueous alkali but dissolves readily in organic solvents. It undergoes most of the typical reactions of the lower alkylated phenols to form ethers, esters, and alkyl, aryl, and halogen derivatives, as well as condensation and hydrogenation products. Owing to the fact that only one of the three normally reactive nuclear positions remains unsubstituted, the compound has a lower reactivity than cresols or xylenols, but is more reactive than hindered phenols such as the isomeric 4-methyl-2,6-di-*tert*-butylphenol. Reaction with formaldehyde or sulfur dichloride gives the expected bis condensation product in each case. Oxidation with persulfate, or nitric or nitrous acids affords the bis compound coupled at the 2-position in each nucleus.

This alkylated phenol is effective as an antioxidant and stabilizer for polyvinyl ethers and related products, and is important through the use of its sulfides, particularly the monosulfide, as reclaiming agents for natural and synthetic rubbers. These compounds accelerate the reclaiming process to a greater extent than other organic sulfides. 3-Methyl-4,6-di-*tert*-butylphenol has been suggested for use in the production of hard rubber or ebonite from butadiene-acrylonitrile copolymers to improve the tensile strength of the ebonite and to increase the tackiness of the stock (9).

4-Methyl-2-*tert*-butylphenol (mono-*tert*-butyl-*p*-cresol), formula weight 164.2, is a colorless crystalline solid. Refined material has the following specifications: mp 51°C; bp 233–241°C; flash point (Pensky-Martens, closed cup) 220°F; vapor pressure (at 100°C) 5 mm Hg; and density 0.930⁷⁰. 4-Methyl-2-*tert*-butylphenol undergoes most of the typical reactions of the lower alkylated phenols. Its sole commercial value at present is for the preparation of condensation products with aldehydes as antioxidants, especially for rubber (9).

4-Methyl-2,6-di-*tert*-butylphenol (2,6-di-*tert*-butyl-*p*-cresol, butylated hydroxy-toluene), formula weight 220.34, is a well-known antioxidant which finds considerable application in a wide variety of industries (9,10). A typical specification for highly purified material is: purity >99%; crystallizing point 69.4°C; flash point (Tag open cup) 260°F; bulk density 37 lb/cu ft; color (molten) APHA scale 30. A free-flowing grade which contains a mineral additive is also available for addition to dry mixes. All grades are available in polyethylene-lined mild-steel or fiber drums and technical material can also be obtained in solution in hydrocarbons in North America.

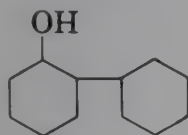
4-Methyl-2,6-di-*tert*-butylphenol is insoluble in water and all strengths of aqueous alkali, but is soluble to varying extent in most common organic solvents. Being a sterically hindered phenol, the compound does not react characteristically for the preparation of phenolates, ethers, esters, and other condensation products; neither does it exhibit the customary phenol coloration with alcoholic ferric chloride solution. Forcing conditions are required for the preparation of the metal phenolates (1) from which it is possible to prepare derivatives such as esters, ethers, and substituted phenoxyacetic acids. In the presence of acid catalysts, such as aluminum chloride, and sulfuric and phosphoric acids, the alkylphenol can be debutylated to produce mono-*tert*-butyl-*p*-cresol, *p*-cresol, and other by-products. Mild oxidation with chromic acid or with bromine converts the 4-methyl group to aldehyde (20,21).

4-Methyl-2,6-di-*tert*-butylphenol is widely used in motor and aviation gasolines, lubricating, turbine, and insulating oils, waxes, natural and synthetic rubbers, paints, plastics, and elastomers; it protects these materials from the effects of atmospheric oxygen during storage and conditions of service. The highly purified grade is suitable for use in foods to delay the oxidative breakdown of animal fats, vegetable oils, and oil-soluble vitamins. It is also used in food-packaging materials—waxed paper, paper-board, and polyethylene. Similarly, it is important for delaying the onset of rancidity in oils and fats in animal feeds and for preserving the essential nutrients and pigment-forming compounds in these feeds. In 1960, production in the U.S. of the technical grade was about 5500 short tons, at a price of about 57¢ per lb, and of the refined grade, 1900 short tons at prices in the range 65¢ to \$1.10 per lb.

2,4-Dimethyl-6-*tert*-butylphenol (6-*tert*-butyl-2,4-xvlenol), is available as technical-grade material (70–80%) for which the following is a typical specification: clear liquid, tending to yellow on exposure; specific gravity 0.956₂₅²⁵; crystallizing point –27°F; bp 250°C; and flash point (Pensky-Martens, closed cup) 230°F.

2,4-Dimethyl-6-*tert*-butylphenol is practically insoluble in water and dilute aqueous alkali, but extremely soluble in the more common organic solvents. It finds wide application as an antioxidant for gasolines and olefins; for inhibiting the premature polymerization of reactive monomers, particularly acrylates and methacrylates; for restricting discoloration during the processing of coumarone-indene resins; and as an antiskinning agent for paints, varnishes, glyceride drying oils, and printing inks (9,22).

***o*-Phenylphenol** (*o*-hydroxybiphenyl),



formula weight 170.2, is a white, crystalline solid with a mild, phenolic odor; crystallizing point 56–57°C; bp 283–286°C; d_4^{20} 1.213; and flash point (closed cup) 257°F. It is obtained as a by-product in the manufacture of phenol by the alkaline hydrolysis of monochlorobenzene but is also produced, in admixture with other phenylphenols, from biphenyl by sulfonation followed by caustic fusion. The U.S. price is 48–50¢ per lb. It is highly soluble in most organic solvents but only sparingly soluble in water. In *o*-phenylphenol, high germicidal activity against a wide range of bacteria and fungi (phenol coefficient, against *Bacillus typhosus*, 48–50) is combined with low toxicity to mammals. It is therefore used as a constituent of disinfectants in soluble cutting oils, and as a preservative for cellulosic and proteinaceous materials including timber, textiles, paper, adhesives, and leather. It is also used as a carrier in the dyeing of polyester fibers. For application in aqueous formulations, *o*-phenylphenol is converted to its sodium salt which is used to control molds and rots of citrus and other fruits and for the disinfection of domestic and agricultural buildings, warehouses, and refrigerated stores (8,9,23).

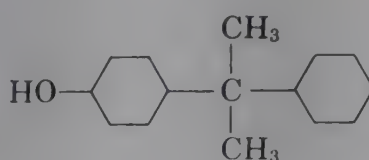
***p*-Phenylphenol** (*p*-hydroxybiphenyl),



formula weight 170.2, is available commercially as a white, flaked solid, mp 159–163°C. It is formed in small amounts in the manufacture of phenol by the reaction of

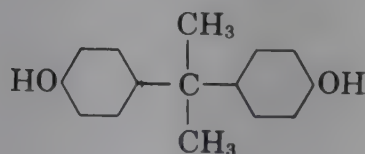
chlorobenzene and sodium hydroxide, and many hundreds of tons yearly are recovered. The U.S. price is about 40¢ per lb. The pure compound has the following specifications: mp 166°C; bp 323°C (220°C at 50 mm); flash point (closed cup) 352°F; specific gravity 1.24₄²⁰. *p*-Phenylphenol is almost completely insoluble in water, but dissolves readily in warm caustic soda solution and is also soluble to an appreciable extent in the common organic solvents such as alcohols, ketones, and ethers. The major commercial use of *p*-phenylphenol is in the manufacture of resins by condensation with formaldehyde. Such resins give varnishes outstanding in durability and in their resistance to moisture and alkalis. Other uses of *p*-phenylphenol are as a dye carrier in the dyeing and printing of polyester fibers; in the preparation of nonionic emulsifying agents; and in the synthesis of dyestuffs. The *o*-chloro derivative, 2-chloro-4-phenylphenol, is used as a general purpose germicide and disinfectant (8,9).

***p*-Cumylphenol** (*p*- α,α -dimethylbenzylphenol),

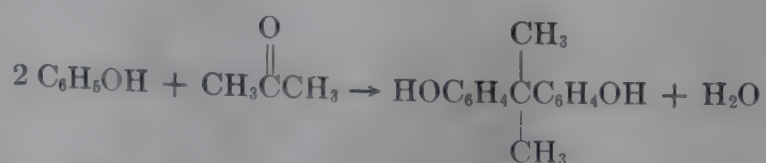


formula weight 212.3, is an almost white crystalline solid; mp 72–73°C; bp 206°C at 20 mm Hg; and flash point (Pensky-Martens, open cup) 355°F. It is practically insoluble in water, but dissolves readily in organic solvents. It is made by reaction of phenol with α -methylstyrene, which is a by-product of the manufacture of phenol by the cumene process; a price of about 35¢ per lb has been suggested. *p*-Cumylphenol gives oil-soluble resins by reaction with formaldehyde, but the varnishes from 100% cumylphenol resins tend to be cloudy. Cloud formation can, however, be overcome by incorporation of minor amounts of certain other alkylphenols at the condensation stage (24,25); the resultant resins are extremely resistant to acids and alkalis, being in this respect almost equivalent to the resin based on *p*-phenylphenol (see p. 911). Other possible uses for *p*-cumylphenol are as an intermediate for the manufacture of dyestuffs, insecticides, and rubber chemicals.

4,4'-Isopropylidenediphenol (2,2-bis(*p*-hydroxyphenyl)propane, bisphenol A),



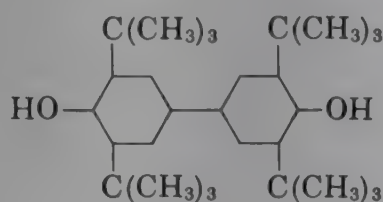
formula weight 228.3, mp 152–153°C, bp 220°C at 4 mm, specific gravity 1.195₂₅²⁵, is available as a white flaked solid. It is only slightly soluble in water, 0.344% at 83°C, but is soluble in ketones and alcohols. It is prepared by the condensation of phenol with acetone under acidic conditions.



Bisphenol A is an important high-tonnage chemical, U.S. production reaching about 25,000 short tons in 1960 at a price of about 27¢ per lb. It is mostly used in the

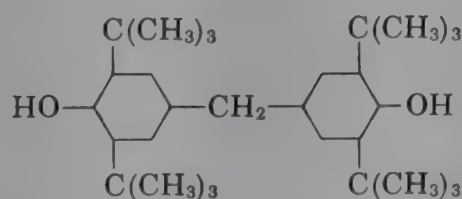
manufacture of epoxy resins and in modified phenolic resins. The most common epoxy resin is produced by reacting bisphenol A with epichlorohydrin; these epoxy resins are used in preparing surface coatings with great resistance to moisture, detergents, and alkalis as well as many other chemicals. Bisphenol A-formaldehyde resins are modified by cooking with rosin or certain ester gums; the resins produced are extremely hard, have a high gloss and melting point, and build viscosity very rapidly. They are used in paints for exterior use, brush enamels, transport finishes, household enamels, and similar products. Nonesterified bisphenol A-formaldehyde resins are used in automobile primers and surface finishes, abrasive binders, office furniture finishes, undercoats, and wrinkle finishes. A new and growing use is in the production of polycarbonate resins. Bisphenol A is also used as an antioxidant in brake fluids and as a stabilizer for polyvinyl chloride resins, oxo alcohols, and their esters. In addition it has shown utility as a fungicide for textiles and asphalt-treated cable covering (26).

4,4'-Bis(2,6-di-*tert*-butylphenol),

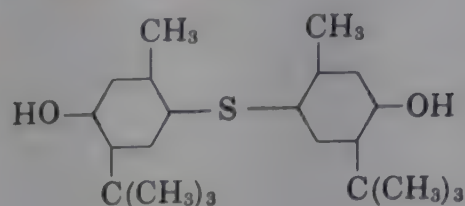


is made from 2,6-di-*tert*-butylphenol, and is commercially available as a light-yellow-colored crystalline solid, formula weight 410.6, and mp 186°C. It is moderately soluble in isopentane and slightly soluble in toluene and ethyl alcohol. It is insoluble in water and 10% aqueous alkali. It is recommended as a high-temperature phenolic antioxidant for petroleum-based oils for high-output engines to inhibit oxidation and bearing corrosion and to minimize scuffing-type piston ring wear. Oxidation control and the prevention of deposit formation in diester-type synthetic oils is claimed, and it is also suggested for improving the thermal stability of jet fuels. As a thermally stable antioxidant of low volatility, it is suggested for use in natural and synthetic rubbers and in polyolefins and waxes (6).

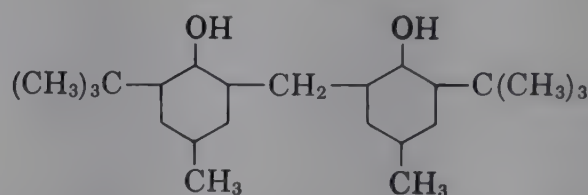
4,4'-Methylenebis(2,6-di-*tert*-butylphenol),



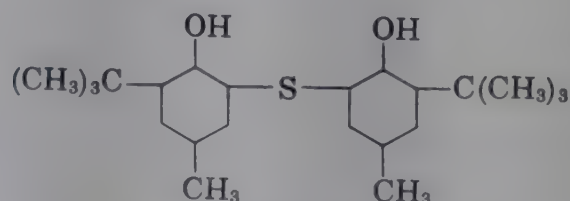
is made by condensation of 2,6-di-*tert*-butylphenol with formaldehyde in the presence of an alkaline catalyst, and is commercially available as a light-straw-colored crystalline solid, formula weight 424.6, and mp 154°C. It is slightly soluble in benzene and petroleum ether and is insoluble in water and 10% aqueous caustic soda. It is recommended as an antioxidant in motor oils for both gasoline and diesel engines. It inhibits oxidation and bearing corrosion. When used alone or with sulfonate or phenolate detergents, it minimizes scuffing-type piston ring wear. It may also be used to inhibit high-temperature oxidation in transmission fluids and industrial oils. Its use is also suggested in natural and synthetic rubbers and in polyolefins and waxes as an oxidation inhibitor (6).

4,4'-Thiobis(3-methyl-6-*tert*-butylphenol),

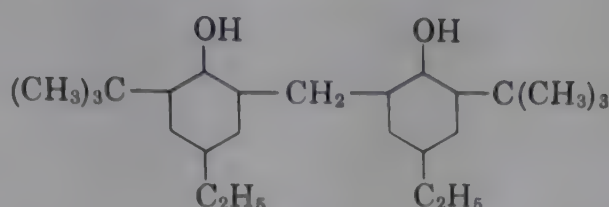
is produced on a scale of hundreds of tons per year and is commercially available as a technical grade, at \$1.55 per lb, and in purified form, as a white crystalline solid, at \$2.80 per lb. The formula weight is 358.29 and mp approximately 161°C. It is moderately soluble in methanol and acetone and very slightly soluble in carbon tetrachloride and ether. It is practically insoluble in water. The compound has high antioxidant activity and finds considerable application in the stabilization of polyethylene and rubber. 4,4'-Thiobis(3-methyl-6-*tert*-butylphenol) has been approved at levels up to 0.05% by the U.S. Food and Drug Administration for use in low-density polyethylene in contact with high water content foods. As a nonstaining and nondiscoloring antioxidant, the compound is recommended at levels of 1 to 2% in light-colored rubbers. It is also recommended in nonstaining neoprene compounds for protection against heat deterioration (27,28).

2,2'-Methylenebis(4-methyl-6-*tert*-butylphenol),

is commercially available in the form of white crystals, molecular weight 340.5, mp 125–133°C. It is soluble in acetone, benzene, chloroform, and most other organic solvents. It is practically insoluble in water. The compound is a particularly good antioxidant for natural rubber and is produced in the U.S. on a scale of several hundreds of tons annually at a price of about \$1.47 per lb. It is claimed to have excellent nonstaining and nondiscoloring properties and is recommended for the protection of light-colored rubber stocks against oxidation. It is claimed to be effective in paraffin wax, fats, and oils, and its use in polyethylene has been suggested (29–31).

2,2'-Thiobis(4-methyl-6-*tert*-butylphenol),

is commercially available as an off-white powder, formula weight 358.29, and melting range 83.0–85.5°C. It is soluble in dioxane, ethylene dichloride, and toluene, and, to a lesser extent, in acetone and ethanol. It is insoluble in water. It is recommended as a nonstaining and nondiscoloring antioxidant for use in polyethylene and rubber and as an antioxidant and corrosion inhibitor in petroleum hydrocarbons. The antioxidant activity of this compound in polyethylene is enhanced by the presence of carbon black (31).

2,2'-Methylenebis(4-ethyl-6-*tert*-butylphenol),

is commercially available as a white solid, formula weight 368.54 and mp 119–125°C. It is soluble in acetone, benzene, chloroform, and many other organic solvents, and is practically insoluble in water. The compound displays little chemical reactivity; it does not react, for example, with bromine water, alkali, or ferric chloride solution. It is used commercially as a rubber antioxidant, especially where freedom from staining is required as in white rubber and latex formulations (30).

Cardanol is a monophenolic mixture obtained by acid treatment and steam distillation of commercial cashew nutshell liquid; boiling range 220–250°C at 10 mm; specific gravity 0.926–0.923²⁵; n_D^{25} 1.5113; and mp < –20°C. It is insoluble in water and dilute alkalies, but is soluble in all common organic solvents. It consists essentially of cardol (6–8%), a resorcinol homolog containing a meta-substituted unsaturated C₁₅ chain, and a mixture (92–94%) of *m*-pentadecyl-, *m*-8-pentadecenyl-, *m*-8,11-pentadecadienyl-, and *m*-8,11,14-pentadecatrienylphenol. Cardanol is used as an ingredient in insulating varnishes and as a plasticizer for laminates. Products obtained from cardanol by polymerization and condensation are used as glues for plywood, as calendering compounds for cloth, as plasticizers for other resins, and as alkali-resistant, oil-soluble blending agents for alkyd resin varnishes, wire enamels, etc. Various esters and ester derivatives are also used as plasticizers.

Hydrocardanol (*m*-pentadecylphenol), C₁₅H₃₁C₆H₄OH, formula weight 304.5, is a white waxy solid; mp 51–51.5°C; bp 380°C (b₁₀240°C); density <1; n_D^{70} 1.4750. It is insoluble in water and in aqueous alkalies, but is very soluble in organic solvents including aliphatic hydrocarbons. It is prepared by the hydrogenation of cardanol. It has been suggested for use as a perfume fixative and as a plasticizer for cellulose acetate lacquers and molding compounds. It can also be reacted with formaldehyde to give resins.

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ALLANTOIN, $C_4H_6N_4O_3$. See Uric acid.

ALLENE, $CH_2=C=CH_2$. See Hydrocarbons.

ALLERGENS; ALLERGY. See Industrial hygiene and toxicology.

ALLITOL, $CH_2OH(CHOH)_4CH_2OH$. See Alcohols, polyhydric.

ALLOSE, $C_6H_{12}O_6$. See Carbohydrates; Sugars.

ALLULOSE, $C_6H_{12}O_6$. See Carbohydrates; Molasses; Sugars.

ALLYL COMPOUNDS

Allyl compounds (from the Latin *allium*, garlic) derive their name from the fact that in common with the chief constituent of oil of garlic, diallyl disulfide $(CH_2=CHCH_2S)_2$, they contain the allyl group, $CH_2=CHCH_2-$. Allyl compounds occur not only in nature, but are important mainly as chemical intermediates and as monomers, especially in the preparation of thermosetting resins. By far the most important allyl compound is allyl chloride (see Chlorocarbons and chlorohydrocarbons), a highly reactive compound which is an intermediate in the preparation of many industrially important substances, including allyl alcohol, glycerol (qv), and epichlorohydrin. Other allyl compounds of considerable importance are allyl alcohol, diallyl phthalate and isophthalate, diethylene glycol bis(allyl carbonate), and triallyl cyanurate. In addition, a number of other allyl compounds enjoy small markets.

Allyl compounds occur widely in nature. Diallyl disulfide and allyl isothiocyanate are the principal constituents of oil of garlic and mustard, respectively. Eugenol, 4-allyl-2-methoxyphenol, is found in many plants, especially in oil of cloves. It is the starting material for a process of synthesizing vanillin. Safrole (4-allyl-1,2-methylenedioxybenzene), is the chief constituent of oil of sassafras. Allyl compounds are commonly found in terpenes, and also occur in steroids and alkaloids.

Physical Properties

Allyl Alcohol (2-propen-1-ol). Allyl alcohol (1), $\text{CH}_2=\text{CHCH}_2\text{OH}$, molecular weight 58.08, is a colorless, mobile liquid of pungent odor. Bp, 96.90, 96.98°C at 760 mm; dt/dp at bp, 0.036°C/mm; mp, -129°C; critical temperature, 271.9°C; d_4^{20} , 0.8520; d_4^{25} , 0.8476; d_{20}^{20} , 0.8535; n_D^{20} , 1.4133; n_D^{25} , 0.4111; vapor pressure, $\log P_{\text{mm}} = 32.62580 - 3451.8/T - 7.94975 \log T$, where $T = 273.15 + t^\circ\text{C}$; viscosity, 0.01486 poise at 15°C, 0.01072 poise at 30°C; surface tension, 24.92 dynes/cm at 30°C; specific heat of vapor, $0.3114 + 0.0007447t$ (t in °C) cal/(°C)(gram); specific heat of liquid, 0.665 cal/(°C)(gram) (average over range 20.5–95.5°C); latent heat of vaporization at 760 mm, 9550 cal/mole.

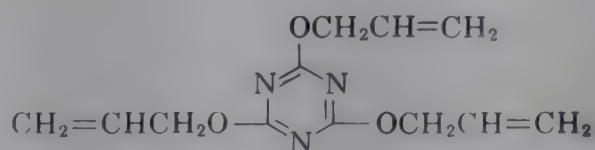
Allyl alcohol is completely miscible with water at room temperature. The constant-boiling mixture with water, boiling at 88.89°C and containing 72.3% allyl alcohol by weight, is the most concentrated solution that can be recovered by distillation of more dilute aqueous solutions. Anhydrous allyl alcohol may be obtained from the constant-boiling mixture by azeotropic distillation with benzene or diallyl ether (composition: 8.7% alcohol, 78.9% ether, 12.4% water). For additional physical properties, including the composition of binary and ternary azeotropes, see reference 1.

Diallyl Phthalate and Isophthalate. Typical properties of commercially available diallyl phthalate and diallyl isophthalate are given below:

	<i>Diallyl phthalate</i>	<i>Diallyl isophthalate</i>
molecular weight	246.35	246.35
bp at 4 mm Hg, °C	161	181.5
mp, °C	-70	-3
n_D^{25}	1.518	1.5212
viscosity at 20°C, poises	0.120	0.169
surface tension at 20°C, dynes/cm	39	35.4

Both esters are insoluble in water and soluble in most organic solvents (24,25).

Triallyl Cyanurate. This compound has a molecular weight of 249.26, and is a colorless liquid or solid. Bp at 2 mm Hg, 162°C; mp, 27.30°C; density, 1.1133 g/ml at 30°C; viscosity, 0.1255 ± 0.0003 poise at 30°C. It has slight solubility in water, and is miscible with acetone, benzene, chloroform, dioxane, ethyl acetate, ethyl alcohol, and xylene (2).



triallyl cyanurate

Diethylene Glycol Bis(Allyl Carbonate) ($\text{O}(\text{CH}_2\text{CH}_2\text{OCOOCH}_2\text{CH}=\text{CH}_2)_2$). Molecular weight 274.3, colorless liquid. Bp at 2 mm Hg, 160°C ; mp, -4 to 0°C ; n_{D}^{20} , 1.4503; d_4^{20} , 1.143; viscosity, 0.09 poise at 25°C . It is insoluble in water and glycerol, but is miscible with ethanol, acetone, ethyl ether, and styrene (3).

Reactions of Allyl Compounds

The double bond activates the functional groups and renders allyl compounds more susceptible to substitution reactions as compared to analogous saturated compounds. This characteristic has made allyl compounds especially useful in organic synthesis. Allyl compounds are also capable of undergoing addition reactions at the double bond and of being involved in rearrangements.

Substitution Reactions (1,4,5). Substitution reactions of allyl compounds involve the replacement of one electronegative functional group by another.



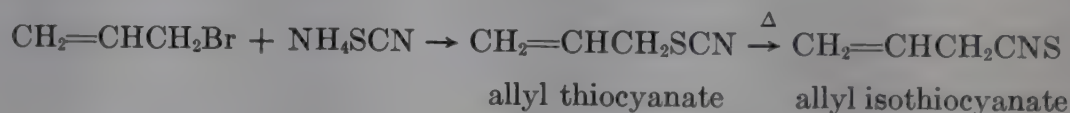
Some examples of this reaction are the conversion of allyl alcohol to allyl chloride,



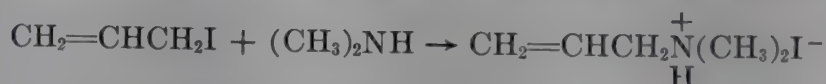
the preparation of allyl ethyl ether from allyl chloride,



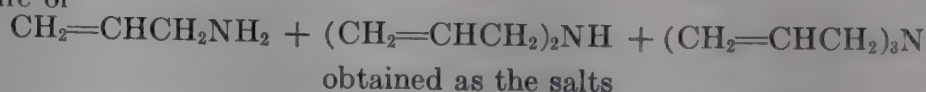
the synthesis of allyl isothiocyanate from allyl bromide,



and the preparation of allylamines from an allyl halide and an amine or ammonia.

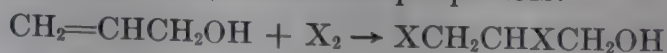


$\text{CH}_2=\text{CHCH}_2\text{Cl} + \text{NH}_3 \rightarrow$ mixture of



Addition Reactions (1,4). Allyl compounds readily undergo addition reactions at the double bond. These reactions are illustrated with allyl alcohol.

Catalytic hydrogenation gives good yields of 1-propanol. Addition of halogens, such as bromine and iodine, gives 2,3-dihalo-1-propanols.

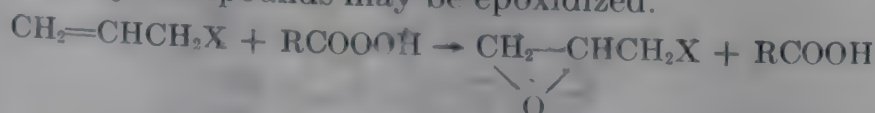


The reaction proceeds in the same way with thiocyanogen to give 2,3-dithiocyano-1-propanol. With chlorine, however, only low yields of 2,3-dichloropropanol are obtained, in some cases because of oxidation of allyl alcohol to acrolein and other products. 2,3-Dihalopropanols may be reacted with sodium hydrosulfide to yield "British anti-lewisite," 2,3-dimercapto-1-propanol.

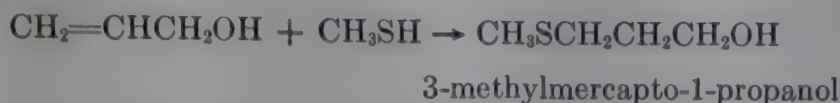
Hypochlorous and hypobromous acids add to the double bond to give a mixture of halohydrins.



The double bond of allyl compounds may be epoxidized.



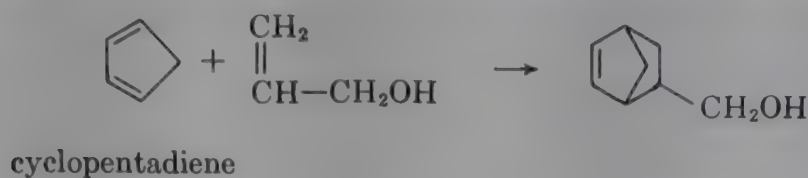
The addition of methyl mercaptan in the presence of mercuric acetate, oxygen, and light has been reported.



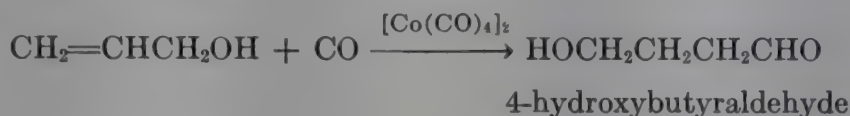
Primary and secondary amines add to the double bond in the presence of sodium to give 3-hydroxypropylamines.



Allyl compounds can participate as dienophiles in the Diels-Alder reaction.



Treatment of an allyl compound with carbon monoxide in the presence of dicobalt octacarbonyl (see Oxo process) gives aldehydes (6).

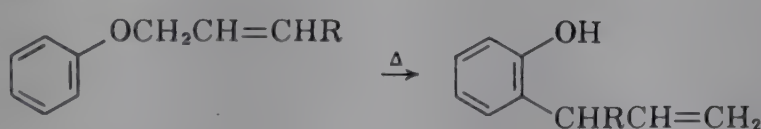


The polymerization of allyl compounds is discussed below.

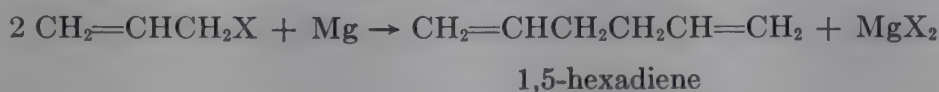
Rearrangements (5). A characteristic of allyl compounds is their ability to undergo rearrangements. This reaction, usually called allylic rearrangement, is observable only in unsymmetrically substituted allyl compounds



where X and Y may be the same or different functional groups. An example of allylic rearrangement is in the Claisen rearrangement of substituted allyl aryl ethers to substituted *o*-allylphenols.



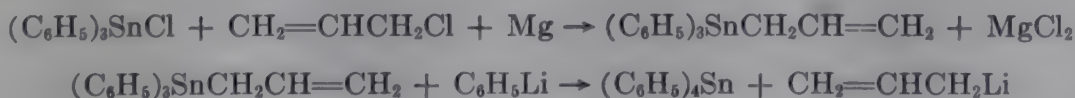
Organometallic Derivatives. Conditions that result in good yields of saturated Grignard reagents give primarily coupling products with allyl halides.



High yields of the Grignard reagent, $\text{CH}_2=\text{CHCH}_2\text{MgX}$, are obtained by the use of a large excess of magnesium and by keeping the concentration of unreacted halide very low (4,5).

Allyl mercuric iodide, $\text{CH}_2=\text{CHCH}_2\text{HgI}$, has been known since 1855. Allyltin compounds and allyl silanes are also easily prepared.

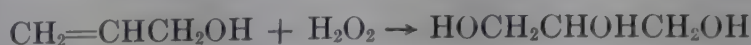
Triphenyltin chloride reacts with allyl chloride in the presence of magnesium to yield allyltriphenyltin, which may be converted to allyllithium (7).



Chemical Properties of Allyl Alcohol (1). In addition to the general reactions of allyl compounds discussed above, allyl alcohol can also undergo oxidation and various reactions of the hydroxyl group. Oxidation in the presence of a metallic catalyst such as copper yields acrolein.



Acrolein also results when allyl alcohol is treated with chlorine under anhydrous conditions. Allyl alcohol may be oxidized to glycerol (qv) using hydrogen peroxide, osmium tetroxide, or other mild oxidizing agents.



More drastic oxidation, such as permanganate under acid condition, yields formic acid.

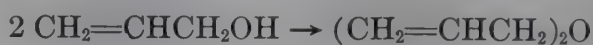


At temperatures of about 300°C in the presence of alumina, zinc oxide, or copper, allyl alcohol is isomerized to propionaldehyde.

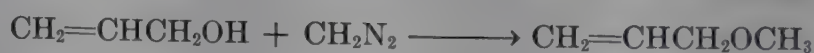
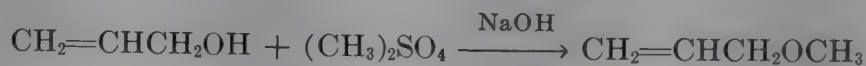


At higher temperatures, allyl alcohol is decomposed to a variety of products including acrolein, hydrogen, carbon monoxide, ethylene, propylene, methane, and acetylene.

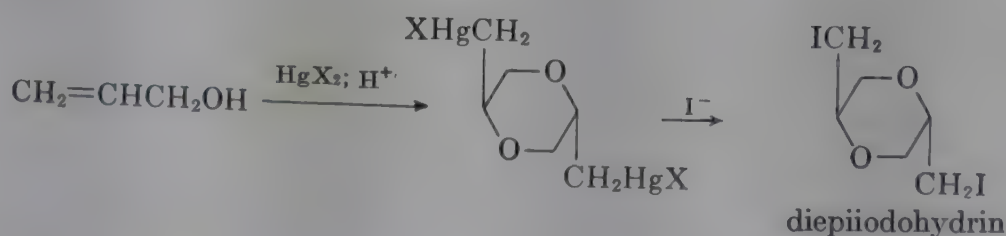
Allyl alcohol may be converted to diallyl ether by acid reagents, such as sulfuric acid, or by catalysts at high temperatures (pumice, 450°C).



Mixed alkyl allyl ethers have been prepared by classical methods such as the reaction of sodium allylate with an alkyl halide. The greater reactivity of the hydroxyl group in allyl alcohol as compared to saturated alcohols permits the use of such reagents as dimethyl sulfate or diazomethane to prepare allyl methyl ether.



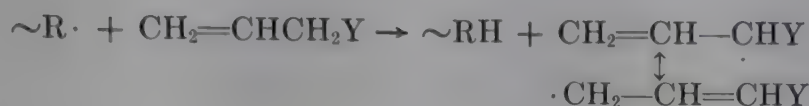
Reaction of allyl alcohol with a mercury salt under acid conditions gives a dioxane which may be converted to "diepiiodohydrin," the structure of which has been shown to be *trans*-2,5-bis(iodomethyl)-*p*-dioxane (8).



The reaction of allyl alcohol with benzene in the presence of Lewis acids gives 1,2-diphenylpropane together with smaller amounts of allylbenzene. With phenols, polymeric products are obtained which depolymerize upon distillation, giving isopropenyl-substituted phenols and coumarans (1).

Allyl alcohol also undergoes the classical reactions of alcohols, such as esterification with both organic and inorganic acids, acetal formation, xanthation, cyanoethylation, carbamate formation, and conversion to a halide (1). Several of the products are useful monomers

Polymerization. Allyl compounds are less reactive in polymerization than vinyl compounds and give, in general, only low-molecular-weight polymers (1,4,9,10); the degree of polymerization rarely exceeds 20. This fact has been ascribed to *degradative chain transfer* wherein active radicals are converted to stabilized radicals which have little tendency to propagate chains. This phenomenon may arise by the abstraction of hydrogen from the allylic position by the growing chain (11,12).



The allyl radical produced is stabilized by resonance and has little tendency to start a new polymer chain by reaction with monomer. A slow rate of reaction and a low degree of polymerization result.

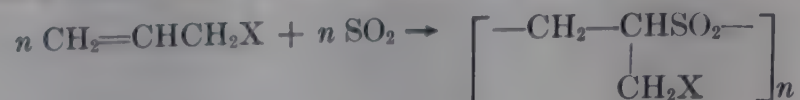
Raising the pressure to 8500 atmospheres increased the rate of polymerization in the case of allyl acetate, but did not raise the degree of polymerization (13). Because of their tendency to undergo chain transfer, allyl monomers may be used as comonomers to reduce the molecular weight in vinyl polymerization. Allyl monomers are best polymerized in bulk and relatively large quantities of catalysts must be used.

Indirect methods may be used to obtain high-molecular-weight allyl compounds. For example, the polymerization of allyl alcohol gives a water-soluble material with a degree of polymerization of only about 5. High-molecular-weight poly(allyl alcohol), insoluble in water, but soluble in methanolic HCl, is obtained by reduction of polyacrolein or poly(methyl acrylate) with lithium aluminum hydride (14). This method has no commercial significance.

Of most importance from the practical point of view are the di- and triallyl compounds which form insoluble, thermosetting resins. Highly crosslinked products with good physical properties may be obtained. Of particular interest is the fact that the di- and triallyl compounds may be polymerized to low conversions to yield soluble, low-molecular-weight prepolymers which have considerable residual unsaturation. These prepolymers can then be converted, in a second step, to thermoset resins. The major advantage of forming a prepolymer is that most of the shrinkage attending polymerization takes place in the first step. Objects of precise dimensions are therefore more easily formed by working with prepolymers. Particularly useful monomers are the polyallyl esters—for example, diallyl phthalate and isophthalate, diallyl maleate, diethylene glycol bis(allyl carbonate), and triallyl cyanurate. Copolymers with unsaturated alkyd resins have also been prepared with these compounds, primarily to impart thermal and chemical stability.

Allyl ethers of polyhydric substances, such as glycerol, pentaerythritol (2,2-bis(hydroxymethyl)-1,3-propanediol) and trimethylolpropane (2-ethyl-2-hydroxymethyl-1,3-propanediol), have additional uses resulting from the presence of hydroxyl groups in the side chains. The hydroxyl groups may be used to form polyesters or reacted with isocyanates to give polyurethans with allyl side chains. Allyl ethers may also be used as components of thermosetting acrylic resins. By reaction through the allylic double bond in a copolymerization with acrylic monomers, the resultant copolymers contain hydroxyl-terminated side chains which may be crosslinked with alkyd resins or urea resins.

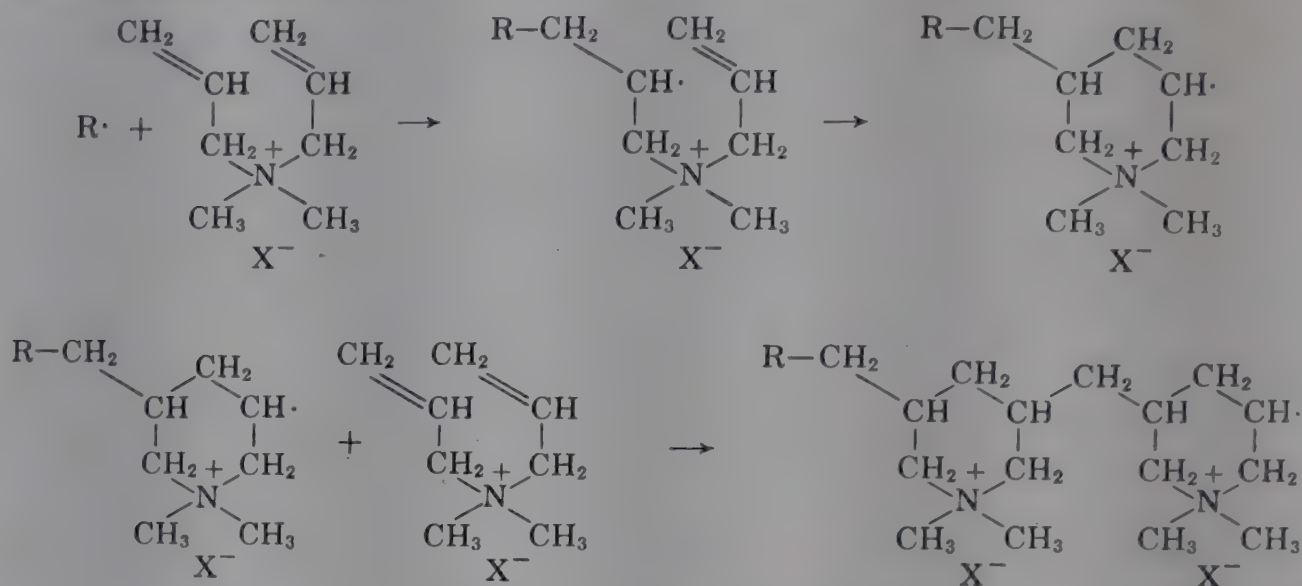
Allyl compounds react with sulfur dioxide to yield polysulfones.



The reaction is initiated by free radicals provided that a certain critical temperature, the "ceiling temperature," is not exceeded (1,4,15).

The polymerization of a number of other allyl compounds, including allylamines and allyl esters of inorganic acids, has also been reported (1,9,10).

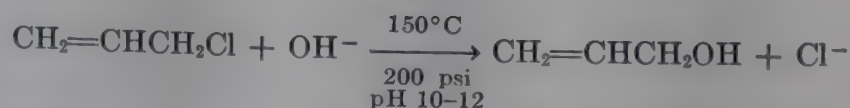
An interesting reaction which may occur with monomers containing two or more allyl groups involves *cyclopolymerization*, wherein both double bonds of the monomer participate in ring formation to yield soluble, noncrosslinked polymers (16,17).



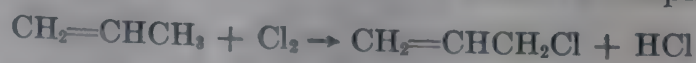
Preparation and Manufacture

Allyl alcohol was first prepared in 1856 by Cahours and Hofmann from allyl iodide, which was derived from glycerol by treatment with phosphorus iodide (1). A more convenient laboratory method consists of heating glycerol with formic acid for 36 hr at 260°C . The alcohol is recovered by distillation (18). This procedure has been adapted to semicommercial production (19).

Industrially, the preferred method of manufacturing allyl alcohol is by saponification of allyl chloride (1,4,20).



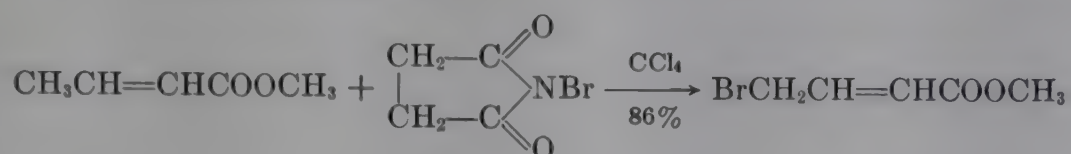
The reaction proceeds readily because of the high reactivity of allyl chloride. The alcohol is recovered by injecting steam to form the water-allyl alcohol azeotrope. Allyl alcohol is dehydrated by distillation with diallyl ether, making use of the ternary azeotrope, and given a final distillation. Allyl chloride is obtained in large-scale production by high-temperature (about 500°C) chlorination of propylene, a process which was discovered in the laboratories of Shell Development Company (4,20).



The preparation of allyl alcohol by catalytic rearrangement of propylene oxide has been described. Alumina and trilithium orthophosphate are reported to be effective catalysts (18,21).

Diallyl phthalate and diallyl isophthalate are made by conventional esterification procedures. Phthalic anhydride and isophthalic acid are the preferred starting materials, respectively. A polymerization inhibitor may be present during reaction (1). Triallyl cyanurate is prepared from cyanuric chloride (NCCl_3) (see Cyanides and cyanogen compounds) and allyl alcohol in the presence of aqueous sodium hydroxide (22). Diethylene glycol bis(allyl carbonate) may be prepared by reacting diethylene glycol, allyl alcohol, and phosgene.

A number of other methods have been reported for the preparation of allylic compounds. They are summarized in reference 5. Particularly noteworthy in synthesis and structure determination is allylic bromination, often called the Wohl-Ziegler reaction. This reaction is normally carried out in carbon tetrachloride using *N*-bromosuccinimide as the brominating agent.



Since light and benzoyl peroxide act as catalysts, the reaction probably involves free radicals (23).

Economic Aspects

Next to allyl chloride (see Chlorocarbons and chlorohydrocarbons), allyl alcohol is the most important allyl compound in commerce.

Large-scale production of allyl alcohol began in the early 1940's when low-cost allyl chloride became available. There are now at least two U.S. companies (Shell Chemical Corporation and Dow Chemical Company) producing a total of several million pounds of allyl alcohol. The price in 1962 was \$0.30 per lb for tank-car quantities. The first large-scale use of allyl alcohol was in the production of diethylene glycol bis(allyl carbonate) which has been produced for about twenty years by the Pittsburgh Plate Glass Company. Present production is approximately several hundred thousand pounds per year, and the price is \$0.81 per lb.

The largest single use of allyl alcohol is in the production of various allyl esters of which diallyl phthalate is the most important. The latter is marketed as the monomer (\$0.51 per lb), as the prepolymer (Dapon 35, FMC Corporation, \$0.85 per lb), and as molding compounds (\$0.81–2.45 per lb). Diallyl isophthalate has a price of \$1.00 per lb for the monomer and \$1.70 for the prepolymer (Dapon M, FMC Corporation).

A number of other allyl compounds are commercially available or under development for potential commercial usage. They include the diallyl ether of trimethylolpropane (Celanese Chemical Company, \$0.785 per lb); diallyl maleate (FMC, \$0.84 per lb); monoallyl ether of trimethylolpropane (Celanese, \$0.885 per lb); mono-, di-, and triallylamine (Shell Chemical Corporation, \$0.96 per lb); allyl bromide (Dow, \$1.50 per lb); triallyl phosphate (Hooker Chemical Corporation, \$1.75 per lb); triallyl cyanurate (American Cyanamid Company, \$1.95 per lb); allyl glycidyl ether (Shell, \$1.965 per lb); diallyl melamine (Cyanamid, \$2.50 per lb); allyl ether of glycerol (Shell, \$2.965); diallyl adipate (FMC); mono- and diallyl itaconate (Chas. Pfizer & Co., Inc.); and triallyl isocyanurate (Allied Chemical Corporation). The total production of the compounds probably does not equal that of the diallyl phthalates at the present time.

Specifications and Analyses

Typical sales specifications for allyl compounds are as follows:

Allyl alcohol

purity	98.0% minimum
specific gravity, 20/20°C (in air)	0.852–0.855
color, Pt-Co(Hazen) standards	15 maximum
distillation range	95.0–98.0°C
water, by weight	0.3% maximum

Allyl alcohol is assayed by an acetylation procedure. The sample is agitated with freshly prepared precipitate of acetylpyridinium chloride, the unused acetyl chloride is hydrolyzed with water, and the resulting acid is titrated to the phenolphthalein end point. Allyl alcohol may also be determined by bromine addition (1). The water content of allyl alcohol is determined by titration with the Karl Fischer reagent.

Diallyl phthalate (24)

specific gravity, 25°C/25°C	1.117 ± 0.003
moisture, ASTM D95–46	0.1% maximum
color, APHA scale, ASTM D268–46/4B	100 maximum
odor	mild

Diallyl isophthalate (25)

specific gravity, 20°C, ASTM D268–46/3	1.124 ± 0.003
acidity, as acetic acid, ASTM D268–46/16	0.05% maximum
moisture, ASTM D95–46	0.05%
color, APHA scale, ASTM D268–46/4B	175 maximum
odor	mild, characteristic

Diethylene glycol bis(allyl carbonate) (3)

assay	94% minimum
specific gravity, 20°C/4°C	1.13–1.15
volatile fraction, bp < 150°C at 5 mm Hg	1% maximum
color, APHA scale	30 maximum
viscosity at 25°C, poises	0.25 maximum

Test methods and standards for allyl molding compounds combined with fillers and pigments have been adopted by the American Society for Testing and Materials (26). Glass-cloth-reinforced polyester laminates modified with diallyl phthalate qualify under Military Specifications Mil-R-7575B, Types I and II.

Health and Safety Factors

Allyl Alcohol (1). Limits of flammability in air, lower limit 2.5%, upper limit 18.0%; flash point, open cup 90°F (32°C), closed cup 72°F (22°C); autoignition temperature in air, 443°C. Allyl alcohol stored at ordinary temperatures is stable.

Allyl alcohol is toxic and its vapor is highly irritating to the respiratory tract and to the eyes. The liquid is readily absorbed through the skin. Symptoms of intoxication may be slow in appearing, but the characteristic odor and lacrimatory effect provide warning. Allyl alcohol should be handled in closed equipment and care must be taken to prevent the liquid from coming in contact with the skin.

Diallyl Phthalate and Diallyl Isophthalate (24,25). These monomers have relatively high flash points, 330°F (166°C) and 340°F (171°C), respectively. They are stable without inhibitors and can be stored indefinitely in closed containers. Neither compound presents unusual physiological hazards if handled with ordinary care.

Triallyl Cyanurate (2). Triallyl cyanurate is a highly reactive monomer which has been known to polymerize violently when heated, particularly in the presence of copper, nickel, manganese, mercury, and their compounds. The commercial product is stabilized with hydroquinone. Triallyl cyanurate is toxic by ingestion, but relatively harmless when administered by other routes of exposure. The compound is not expected to present a health hazard under normal circumstances of industrial handling.

Diethylene Glycol Bis(Allyl Carbonate) (3). This product has a flash point of 378°F (177°C). It is relatively stable in storage at ordinary temperatures.

Uses

Allyl compounds have a wide range of uses. Allyl alcohol is a useful intermediate, especially in the preparation of allyl ethers and esters, and has been used to control weeds (27), nematodes (28), and fungi (27,29). Allyl esters are important monomers and have also found markets in perfumery. Many naturally occurring allyl compounds are food flavoring agents. Safrole may be converted into piperonal which is used in the perfume industry. A number of allyl derivatives of barbituric acid are sold as narcotics. Sodium allyl sulfonate improves the ductility and brightness of nickel in electroplating (30). Allyl alkylxanthates are excellent promoters in the flotation of copper sulfide ores (31).

The single most important use of allyl compounds is in the preparation of polymers. Allyl monomers generally have good stability and, in many cases, may be converted under relatively mild conditions to crosslinked, thermoset resins. No water is

Table 1. Typical Properties of Castings of Diethylene Glycol Bis(Allyl Carbonate) Polymer (32)

specific gravity, 25°C	1.32
refractive index	
n_D^{20}	1.504
n_C^{20}	1.501
n_F^{20}	1.510
dispersion factor, $\frac{n_D - 1}{n_F - n_C}$	57.8
light transmission, 1/4 in., %	89-92
Rockwell hardness	M95-M100
tensile strength, psi	5,000-6,000
modulus of elasticity in flexure, 25°C, psi	$2.5-3.3 \times 10^6$
compressive strength, psi	22,500
Izod impact strength, 25°C, ft-lb/in. notch	0.2-0.4
heat distortion temperature, 10 mils, °C	60-75
maximum recommended operating temperature, °C	
continuous service	100
intermittent service	150

evolved during the polymerization, which is a definite advantage over thermosetting resins of the condensation type.

One of the earliest allyl monomers to achieve commercial significance was diethylene glycol bis(allyl carbonate). This compound, sold under the trade name Allymer CR-39, upon polymerization forms clear castings which have good optical

properties and high scratch resistance (see Table 1) (32). It has been used in aircraft nose bubbles, safety goggles, and sunglasses. Its temperature resistance can be improved by copolymerization with triallyl cyanurate (33).

Triallyl cyanurate is particularly useful as a comonomer with unsaturated polyesters. Laminates made from these resins with glass cloth retain excellent strength even at 500°F, and have good chemical resistance. Triallyl cyanurate may also be copolymerized with methyl methacrylate (34) to give hard, stable resins with excellent optical properties (2).

The most widely used allyl monomer is diallyl phthalate. Because of its good stability, low volatility, lack of noxious odor, and high flash point, it can be handled conveniently. It is being used as a crosslinking agent for unsaturated polyesters to impart heat and dimensional stability and resistance to chemicals. Shrinkage on polymerization is 30% less than with styrene, permitting easier molding of parts with close dimensional tolerances (35). Diallyl phthalate polyester systems are widely used in the fabrication of glass-reinforced industrial laminates, especially for radomes.

When diallyl phthalate is polymerized with a peroxide catalyst under carefully controlled conditions, it is converted to a white powder having residual unsaturation. This prepolymer is sold commercially under the name of Dapon diallyl phthalate resin (36). Dapon resins may be cured to a highly crosslinked thermoset material by the application of heat under standard molding conditions. Peroxide catalyst may also be used. Shrinkage is less than 1% during cure. The cured resins have excellent dimensional stability, insulation resistance, dielectric strength, and resistance to chemicals. These properties are largely retained upon exposure to high temperature and high humidity conditions. Typical properties of molded diallyl phthalate resin, both unfilled and reinforced, are given in Table 2. Diallyl isophthalate resins, sold

Table 2. Typical Properties of Diallyl Phthalate Polymer (36)

Property	ASTM test method	Unfilled	Acrylic fiber filled	Glass fiber filled
molding temperature, °F		270-320	270-320	270-320
molding pressure, psi				
compression		500-2,000	500-3,000	500-2,000
transfer			1,000-8,000	1,000-8,000
flexural strength, psi	D790	7,000-9,000	10,000	18,000
Izod impact strength, ft-lb/in. notch	D256	0.3	1.2	6.0
mold shrinkage, in./in.	D955		0.009	0.002
heat distortion point, °F	D648	310	265	392
continuous heat resistance, °F	D794	350	300	450
dielectric strength, v/mil				
short time	D149		350-400	335-400
step-by-step	D149	450	275-350	300-420
volume resistivity, ohm-cm	D257	1.8×10^{16}	1×10^{16}	1×10^{15}
dielectric constant	D150			
60 cycles		3.6	3.8	4.3
10 ³ cycles		3.6	3.7-4.0	4.2
10 ⁶ cycles		3.4	3.3-3.6	4.3
dissipation factor	D150			
60 cycles		0.010	0.026	0.01
10 ³ cycles		0.009	0.020-0.025	0.004
10 ⁶ cycles		0.011	0.015-0.020	0.01
arc resistance, sec	D495	118	85-115	125

under the trade name Dapon M, have similar properties, but higher operating temperatures (450–500°F) may be employed than for phthalate resin. The combination of desirable properties has led to wide use of Dapon resins in molding and encapsulating of electrical parts, especially for aerospace applications, as in radomes, molded circuit panels, miniature capacitor cases, potentiometers, and connectors (36).

Diallyl phthalate is also finding increasing markets in low-cost decorative laminates for furniture. A resin-impregnated overlay and paper printed with the desired pattern can be laminated at low pressures (100–250 psi at 300–350°F) on inexpensive core materials, such as particle board, to produce attractive products with good resistance to chemicals, heat, and abrasion. The overlay is generally made of acrylic fiber which becomes transparent during the curing process. The same technique, but without the printed paper can be used to make a protective coating on wood veneers (37).

The utility of allyl ethers in coatings has been known for many years. Originally allyl ethers of sucrose and starch were used (38), but they have largely been displaced by other materials, including ethers of pentaerythritol and trimethylolpropane (39–41). Polyurethan elastomers that may be cured with sulfur are obtained using allyl ethers of polyols (42). The addition of 0.003–0.3% of diallyl ether in the polymerization of vinyl chloride has been claimed to give improved mechanical properties (43). Copolymers of diallylammonium compounds with acrylamide and acrylonitrile increase the strength of paper (17). Polymers of various allyl phosphates and phosphonates impart flame resistance to cellulose. Triallyl phosphate is especially effective when polymerized using bromoform as a chain-transfer agent (9).

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ALLYLAMINE, $\text{CH}_2=\text{CHCH}_2\text{NH}_2$. See Amines.

ALMOND OIL. See Benzaldehyde; Oils, essential.

ALOE; ALOIN, $\text{C}_{20}\text{H}_{18}\text{O}_9$. See Cathartics.

ALPHA-NAPHTHOL; ALPHA-NAPHTHYLAMINE. See Naphthalene derivatives.

ALTROSE, $\text{C}_6\text{H}_{12}\text{O}_6$. See Carbohydrates; Sugars.

ALUM. See Aluminum sulfate and alums under Aluminum compounds.

ALUMINA, Al_2O_3 . See Aluminum oxide under Aluminum compounds.

ALUMINATES. See Aluminum compounds.

ALUMINOSILICATES. See Silica and inorganic silicates.

ALUMINUM AND ALUMINUM ALLOYS

Economic aspects.....	929	Aluminum and its alloys.....	954
Raw materials.....	931	Heat treatments.....	968
Manufacture of alumina.....	937	Fabrication of aluminum alloys.....	971
Electrolysis of alumina.....	941	Corrosion.....	977
Other processes for obtaining aluminum	944	Surface treatments.....	978
Very pure aluminum by electrolytic re-		Uses.....	982
fining.....	946	Test methods.....	987
Properties of aluminum.....	948		

The existence of aluminum had been predicted by the end of the eighteenth century. As a sequel to the studies made by the Englishman Davy (1808), the Dane Oersted (1821), and the German Woehler (1827), it was the Frenchman Sainte-Claire Deville who, in 1854, realized the first method for producing the metal industrially by chemical means. But this method, based on the use of sodium to reduce the double chloride of aluminum and sodium, was too involved to allow development on a truly industrial scale.

Apart from this chemical process, Sainte-Claire Deville had in mind from 1854 onward a way of producing aluminum electrolytically by the decomposition of a molten mixture of aluminum chloride and sodium chloride. The real key to the industrial manufacture of aluminum by electrolytic means, however, was the substitution of Gramme's dynamo for the galvanic battery as a source of current. The electrolytic process was discovered simultaneously in the United States by Hall and in France by Hérault in 1886. In this process, which is still in use today and which provided the basis for the development of aluminum, a bath consisting of alumina dissolved in fused cryolite is decomposed by electrolysis. In order to prevent the metal from taking up nearly all the impurities of the alumina, the first, and very important, stage in producing aluminum is to prepare anhydrous alumina from the ore in as pure a form as possible.

However, other processes are presently being studied. One of these, in France, is based on the carbothermic reduction of aluminum oxide; the other, in Canada, on direct reduction followed by distillation. As these methods tie up less capital than does the electrolytic process, they may prove to be the starting point for a new upswing in the use of this metal (1).

Economic Aspects

The tremendous growth of the aluminum industry, as compared with that of the other principal nonferrous metals, is shown in Table 1.

The aluminum industry originated in countries disposing of two types of natural resources: bauxite mines (bauxite is the main aluminum ore) and—even more important—cheap electrical energy, such as may be obtained from hydroelectric power plants.

Table 1. World Production of Aluminum, Copper, Lead, and Zinc, in thousands of metric tons (2204 lb)

Year	Al	Cu	Pb	Zn
1900	5.7	499	877	479
1960	4,670	4,400	2,630	3,070

Table 2. World Production of Aluminum

Country	Production, metric tons		Estimate for 1965 (minimum)
	1938	1960	
U.S.A.	139,000	1,828,000	2,500,000
Canada	66,000	691,000	1,250,000
Miscellaneous		19,000	165,000
<i>Total for the Americas</i>	<i>205,000</i>	<i>2,538,000</i>	<i>3,915,000</i>
France	45,300	235,000	350,000
German Federal Republic	161,200	169,000	245,000
Norway	29,000	165,000	300,000
Italy	25,800	84,000	130,000
Austria	4,400	68,000	75,000
Switzerland	26,000	40,000	45,000
United Kingdom	23,400	29,000	35,000
Yugoslavia	1,300	25,000	85,000
Sweden	2,300	15,000	15,000
Spain	800	29,000	54,000
Greece			50,000
<i>Total for Western Europe</i>	<i>319,500</i>	<i>859,000</i>	<i>1,384,000</i>
U.S.S.R.	48,000	800,000	1,800,000
People's Republic of China		75,000	180,000
German Democratic Republic		40,000	55,000
Hungary	1,500	50,000	60,000
Poland		25,000	74,000
Czechoslovakia		57,000	50,000
Rumania and Bulgaria		10,000	25,000
<i>Total for Eastern Countries</i>	<i>49,500</i>	<i>1,057,000</i>	<i>2,244,000</i>
<i>Other Asian Countries (Japan, Taiwan, India)</i>	<i>27,900</i>	<i>160,000</i>	<i>345,000</i>
<i>Africa</i>		<i>44,000</i>	<i>95,000</i>
<i>Australia</i>		<i>12,000</i>	<i>28,000</i>
<i>Total World Production</i>	<i>601,900</i>	<i>4,670,000</i>	<i>8,011,000</i>

Table 2 shows variations in the aluminum output of different countries just before World War II and at present, as well as forecasts for the development of this industry in future years.

Obviously the last war, in which aircraft were constructed from light metals (up to 80% of their structural weight) played a leading role and gave special impetus to the industry.

Whereas, in 1938, none of the factories producing aluminum had a capacity of more than 50,000 tons a year, the one at Arvida in Canada can now produce 330,000 (short) tons a year. The plant at Kitimat in British Columbia is designed for 500,000 tons a year. In the United States there is a plant which can produce 247,500 tons annually and others which can produce 100,000 tons each. In Europe the largest factory, at Noguères, France, can turn out 90,000 (metric) tons a year. Special mention should be made of the recent entry of the African continent into aluminum production. In 1957 the works at Edea in the Cameroons started with a capacity of 45,000 tons of aluminum per year. In Guinea, at Fria near Konkouré, a plant capable of making 480,000 tons of alumina per year and of expanding further came into operation during 1960. Major projects depending on electrolysis are possible in Africa by reason of the enormous local hydroelectric power potentialities; the most

important of these is being envisaged at Inga in the Congo (Léopoldville), while Ghana recently seemed close to completing a 200,000-ton project. Guinea, the Congo (Brazzaville), and Angola are some of the countries offering still other opportunities.

The increased capacity of the plants and electrolytic cells in use, and the progress made in methods of manufacture, have improved the productivity and diminished the consumption of electric power. Between 1938 and 1959 the savings realized have amounted to 78% in the use of labor, and to 25% in the use of energy. This led to a considerable lowering in price (see Table 3).

Table 3. Comparative Prices, ¢ per lb

Metal	1900	1938	1960	
			In today's currency	In currency stabilized at the 1938 value
Copper	16.5	10.1	32.2	15.5
Aluminum	32.7	20.0	26.0	12.5

It is as yet too early to anticipate the price of aluminum that will result from the adoption of modern chemical and electrothermal processes.

Consumption has developed in step with production, reaching in 1959 the following annual averages per head of population in the various countries:

Table 4. Per Capita Consumption of Aluminum in 1959

Country	Kilogram
U.S.A.	11.3
Switzerland, Norway	6.8
Great Britain, Belgium	5.6
France, Sweden, Austria, Germany	4.0-4.5
Denmark, Italy	1.4-1.8

Thus, it is reasonable to assume that the world consumption of aluminum will continue to increase greatly. This accounts for the metal's great importance (2).

Raw Materials

Bauxite is the principal ore of aluminum. It consists of aluminum oxide, more or less hydrated and containing various impurities, such as iron oxide, aluminum silicate, titanium dioxide, quartz, and compounds of phosphorus and vanadium (see also Clay).

Thus, bauxite cannot be regarded as a definite mineralogical species; however, it has become customary to use this term for rocks of mineral deposits in which alumina preponderates, ever since a French chemist, Berthier, discovered in 1821 the first deposits of this kind, close to the picturesque village of Les Baux in Provence.

There are many varieties of bauxite and these varieties may occur in many different forms. The principal classification of bauxites depends on the degree of hydration of the alumina they contain, and on this basis the following may be distinguished: (1) *Monohydrate bauxites*, which contain the hydrated alumina $AlO(OH)$, and which take two distinct mineralogical forms, known as boehmite and diaspore,

respectively. (2) *Trihydrate bauxites*, in which the alumina takes the form $\text{Al}(\text{OH})_3$, and which are known as gibbsite or hydrargillite. (See also Aluminum oxide under Aluminum compounds.)

This classification is of great practical importance in processing, as the methods used to treat bauxites in order to extract pure alumina are based on attacking the bauxites with caustic soda and as the aluminum trihydrate is much more soluble in that alkali than are the monohydrates.

Generally speaking, the bauxites found in countries with a temperate climate, especially in European countries, are of the monohydrate type, whereas those found in tropical countries are of the trihydrate type. This, however, is by no means an absolute rule, for in each case there are mixed bauxites wherein the two kinds of hydrates are combined, but the local type predominates in the mixture.

Deposits of bauxite owe their origin to siliceous rocks from which the silica and other components except alumina have been more or less leached out; but this transformation took place at different geological epochs, depending on the position of the mineral beds. The deposits in Mediterranean Europe, which were the first to be discovered and exploited, are the oldest. They lie on limestone formations ranging from the Jurassic to the Eocene, and it is assumed that they derive from the desilication of clay particles which were present as impurities in primitive limestones. The deposits in tropical countries, which may be of more recent formation, result from a particular kind of decomposition by weathering (laterization) of basement (or primary) rocks, such as micaschists, basalts, syenites, dolerites, etc. Bauxite is a laterite which contains preponderantly alumina.

During the last few decades considerable quantities of bauxite were discovered in many of the tropical countries, contrary to the assumption made in the early years of the aluminum industry that this mineral was peculiar to southern France and to certain countries in the south of Europe.

The suitability of a bauxite as a raw material for aluminum extraction depends not only on its alumina content but also, and especially so, on its content of combined silica in the form of kaolinite. Not only does such a silica, if present, tie up a certain amount of alumina that cannot be extracted, but in the course of treatment it entails a heavy and expensive loss in insolubilized caustic soda. Roughly speaking, each kilogram of SiO_2 involves the loss of 1 kg of Al_2O_3 and 0.6–0.7 kg of Na_2O .

The composition of the bauxites used in aluminum manufacture varies a great deal, each country having to make the best of whatever deposits it has, but the variations generally fall within the following limits:

Table 5. Typical Composition of Bauxites for Aluminum Manufacture

Composition	Percent
H_2O , combined	12 to 30
Al_2O_3 , total	40 to 60
SiO_2 , free and combined	1 to 15
Fe_2O_3	7 to 30
TiO_2	3 to 4
F, P_2O_5 , V_2O_5 , etc	0.05 to 0.20

Apart from its use for the extraction of alumina, bauxite serves various secondary purposes, the principal ones being the manufacture of refractories and of aluminous

cements. In small quantities, bauxite is also employed (as is or in a form activated by dehydration) as either a catalyst or a drying agent in the chemical and petroleum industries. (See also Aluminum oxide under Aluminum compounds.)

WORLD DISTRIBUTION OF BAUXITE

In order to present a concise survey of world bauxite deposits, each of the continents is being considered below, in chronological order as to the discovery and exploitation of bauxite deposits.

Europe. As already stated, the first bauxite deposits were discovered in France, where they were utilized as of 1860. Later other European beds were found which, not counting some rare exceptions, had been deposited in the Cretaceous period over the limestones forming the northern edge of the ancient Mediterranean basin. This bauxite is of the monohydrate type, generally boehmite but, in the eastern part of the basin, occasionally diaspore.

France. Close to the Mediterranean shore, three groups of deposits may be distinguished, as follows: (1) In the Department of the Var, in the district of Brignoles, the best deposits as regards both quantity and quality have been found and worked; these were the key to the development of the European aluminum industry in the first decade of this century. (2) In the Department of Hérault, there are deposits in the regions of Bédarieux and Villeveyrac. (3) In the Department of Bouches-du-Rhône, the aforementioned deposits occur in the Baux region.

As the beds with low silica content were the earliest to be worked, the silica (SiO_2) content of those which are presently being mined is increasing continually and most of the workings take place underground.

Including those beds which have a relatively high silica content—a condition with which the aluminum industry is now able to cope—the French reserves exceed one-hundred million tons in all. They are being used almost exclusively in the French aluminum factories.

Spain. In the north of Catalonia, at the edge of the Pyrenees, there are some millions of tons of as yet unexploited siliceous deposits (containing 8 to 15% SiO_2).

Italy. Two deposits amounting to some millions of tons, in the Appennines and in Puglia, partially supply the Italian factories.

Yugoslavia. Large deposits exist in Istria, in Dalmatia, in Herzegovina, and, discovered more recently, in Montenegro. The total Yugoslavian reserves may thus be approaching one-hundred million tons. Most of what is mined in that country is exported to Germany and Italy, but a local aluminum industry is being developed.

Austria. There is one notable deposit, amounting to some millions of tons of a siliceous mineral.

Hungary. Very large deposits, of variable quality, exist on the spurs of the Alps; they often contain much water and a large trihydrate component. Total Hungarian reserves probably exceed one-hundred million tons. Aluminum factories in Hungary are being developed actively and the exports to the Soviet Union are important in the form of either bauxite or alumina.

Rumania. There are deposits containing some 10- to 20-million tons of very hard bauxite, rich in diaspore, but they are not yet being exploited.

Greece. Two very large deposits exist on the northern side of the Gulf of Corinth. These reserves comprise approximately 50 to 100 million tons of a bauxite containing a

high proportion of diaspore. Large quantities of bauxite are exported to Western Germany and to the Soviet Union. Local processing is being projected.

Turkey. The beds identified in Asiatic Turkey (in the Taunus range) are connected with those of the Mediterranean basin. They contain some tens of millions of tons, of mixed quality, and are not exploited.

North and South America. Important deposits exist in the tropical zone, mainly north of the equator.

United States. There is an important deposit in Arkansas where the reserves may amount to some 50-million tons. Here the bauxite is of the trihydrate type and rather rich in silica (8 to 15% of SiO_2). The utilization of this bauxite, since World War II, has necessitated introducing an additional step in the usual processing. This deposit fills about 20 to 25% of the present U.S. requirements of alumina. There is another bauxite-containing region in northwestern Oregon but these deposits are not being worked as the ore is of poor quality.

The Guianas. British Guiana and Dutch Guiana (Surinam) have considerable deposits of high-quality tropical bauxites which are being worked very intensively and which, until recent years, have supplied most of the needs of the aluminum industry of North America (U.S.A. and Canada). As in most tropical deposits of recent formation, the bauxite occurs in thick surface layers, ranging from 4 to 12 m; these layers are covered over with clay and sand of varying thickness, in this case generally between 1 and 30 m.

In these two Guianas, the reserves may amount to several hundred million tons and their exploitation continues to be very active. Often the ore is subjected to a beneficiation process in order to reduce the silica content. More recently, a bed containing some 40-million tons has been discovered in French Guiana, but the quality of the ore is lower than that of the neighboring Guianas and the deposit is not yet being worked.

Carribean Islands. Since the last world war important deposits have been found in the Dominican Republic, Haiti and, especially, Jamaica. In Jamaica, bauxites of a very fine texture have formed deposits on marine limestones, in layers 3 to 10 m thick, where they are covered with very little organic soil or other overburden. These reserves may amount to some 300-million tons.

These deposits are now being exploited for export to the U.S., but two alumina plants have been installed locally for supplying alumina to Canada. The deposits in Haiti and in the Dominican Republic are much less extensive, amounting to no more than 5- to 10-million tons.

Brazil. The estimates advanced for a number of scattered deposits total 100- to 150-million tons. As yet there is very little information about the regions of the Amazon.

Miscellaneous. Venezuela and Costa Rica have been reported to possess deposits of some importance.

Union of Soviet Socialist Republics. The first deposit to be exploited, from 1930 onward, was a small one containing 4- to 5-million tons of not very good quality, at Tikhvine some 200 km west of Leningrad.

Since that time important deposits have been discovered and are being exploited in the Urals. These bauxites are of the monohydrate type, sometimes containing diaspore; their quality varies and they tend to be siliceous. In Siberia very large deposits have been found, for instance, in the eastern part of Kazakstan, in the

Turgay region, and in the northern part of Mongolia. Considerable tonnages would appear to be available but the quality is poor and the silica content ranges up to 15%.

In view of its insufficient resources in bauxite, as regards both quantity and quality, the U.S.S.R. has directed a large part of its aluminum industry to the extraction of alumina from nepheline, the double silicate of aluminum and of an alkali metal (Na or K). This treatment is complicated and expensive but it yields important by-products in the form of cement and of alkaline carbonates. The first plant designed for this process was based on the nephelines that occur jointly with phosphates in the Kola peninsula, which lies in the north of European Russia. A second very large plant is being developed on the site of nepheline deposits in Siberia.

Africa. In Africa, where the laterite zones cover immense areas, considerable deposits of bauxite have been discovered during the last ten years and it can now be said that this continent possesses a large share of the world's reserves of this mineral.

Republic of Guinea (formerly French Guinea). In the Los Islands, some four kilometers from Conakry, a deposit amounting to a few million tons is being exploited for export to Canada. This source is gradually being exhausted, but the more important deposits are those of the interior. They are divided between the following three regions:

1. The Conakry region, within a radius of 150 km around Conakry, contains two deposits, that of Kindia (along the Conakry-Niger railway) and that of the lower Konkouré (on the Fria and Kimbo plateaux).

Taken together, these constitute a reserve of approximately 200-million tons of a mineral containing little silica, but rich in Fe_2O_3 , which cannot easily bear the cost of export. A big alumina plant has been set up at Fria, the production from which is exported to the Cameroons, to Europe, and to the United States. The hydroelectric possibilities of the Konkouré would also permit large quantities of aluminum to be produced locally.

2. The Boké region, situated at about 100 km from the northern coast of Guinea, contains deposits amounting to several hundreds of millions of tons. Prospecting has yielded bauxite of excellent quality, that could be exported. These deposits extend northward into Portuguese Guinea.

3. The Fouta Djallon region (at several points on the high plateaux of the Fouta-Djallon—close to Dabola-Tougué) possesses several deposits which have recently been prospected and which collectively make up some hundreds of millions of tons. These lie more than 500 km from the port of Conakry by the Conakry-Niger railway.

Mali (formerly French Sudan). Close to the northeastern frontier of Guinea, west of Bamako, large deposits have been found which contain little silica but are rich in Fe_2O_3 .

Ghana (formerly the British colony of the Gold Coast). Located 150 to 200 km from the coast, on the high plateaux of the Volta basin, there are various deposits estimated at 200-million tons, which have been partially exploited for export to Britain and Germany. An important project utilizing electric power from the Volta is being carried out to the aluminum stage for purposes of local exploitation.

Cameroons. A very important deposit was discovered in 1958, close to Tibati, on plateaux which lie 1700 to 1800 m above sea level to the northeast of the Cameroons, 450 km (as the crow flies) from the port of Duala. These reserves are estimated at several hundreds of millions of tons. Nearer the coast, approximately 150 km from Duala, a smaller deposit containing some tens of millions of tons is known to exist.

Congo Republic (formerly the Belgian Congo). Close to the estuary of the Congo river and 100 km north from the port of Matadi a deposit of some tens of millions of tons has been prospected. In spite of some unfavorable features, this deposit might hold some economic interest because of its proximity to the Inga site on the Congo, where there are considerable hydroelectric potentialities.

Miscellaneous. Smaller deposits have been found in Nyasaland (60-million tons) and in Mozambique and Madagascar (a few million tons).

Asia. Apart from the deposits in the U.S.S.R. and in Turkey, which have already been mentioned, the known Asiatic deposits are those which are found in the southern part of the continent. These are generally of the tropical type.

India. Among the many lateritic formations which exist in India there are various bauxitic zones which, taken together, may probably constitute reserves adding up to 100- or 200-millions of tons.

Malaysia and Indonesia. In the Malay peninsula and in its extension, the Riouw archipelago, which forms part of Indonesia, there are several deposits that add up to some tens of millions of tons. Indications of some others have been reported from Borneo. The deposits in Malaysia and Indonesia supply the Japanese aluminum industry.

Tonkin. A small deposit of diasporous bauxite exists to the north of Haiphong.

China. In Yunnan a small deposit of a type similar to the one at Tonkin is known to exist. In the province of Kweichow there are believed to be some tens of millions of tons of diasporous bauxite. In what used to be called Manchuria, schists rich in both alumina and silica have been exploited. The whole of central China, however, seems to have been little prospected and may be a source of surprises.

Australia. During recent years very large deposits have been discovered in several regions, which make Australia a world reserve of bauxite of the first importance, of the order of approximately a thousand million tons.

The most important of these are (1) in the north of Australia, those on the west coast of the Cape York peninsula, near Weipa, and those on the Cove peninsula (Arnhem Land), which lies to the west of the Gulf of Carpentaria; (2) in the southwest, the deposits around Perth.

The main world producers of aluminum are interested in the economic potential of these deposits. The production of the metal might be carried out in New Zealand, which has great possibilities for the use of electric power, and where there is already one small aluminum factory.

CRYOLITE

At the beginning of the aluminum industry, the manufacturers employed the natural ore called cryolite, $\text{AlF}_3 \cdot 3\text{NaF}$. The rarity of this ore, however, rapidly caused the industry to produce synthetic cryolite.

The natural cryolite is used primarily for starting an aluminum cell. During the operation mainly synthetic cryolite is employed in order to obtain a slightly acidic electrolytic bath, with the necessary small excess of AlF_3 .

A white mineral of monoclinic crystalline form, cryolite undergoes a reversible crystalline change at 565°C . Melting point is 1006°C ; heat of fusion, $73.8\text{--}79.2$ cal/g; and specific heat (fused), 0.38 cal/g/ $^\circ\text{C}$.

Natural cryolite is found in beds situated in the ancient Danish colony of Greenland. The excavating site is in the Godthaab district, at Ivitgut on the south coast

of the Arsukfjord, in the southwestern part of the island. The mineral is found in veins imbedded in granite, which is covered with gneiss. The exploitation is made in the open air and can be carried out during the short period of the Arctic summer. It is controlled by the Kryolit Selskebt Øresund A.S., a Danish company created in February 1859. The production capacity is approximately 30,000 (metric) tons a year.

The ore is exported either to Denmark or to the United States. Other countries receive the mineral after processing. The composition is approximately the following:

Table 6. Typical Composition of Cryolite

Composition	Percent
F	51
Al ₂ O ₃	12.5
Na	30
SiO ₂	0.30
Loss on roasting	0.15

Synthetic cryolite may be produced by several methods that have been suggested, by either dry or wet processes, but it seems that the latter type has prevailed. The wet process is based on the action of hydrofluoric acid on sodium aluminate, according to the equation



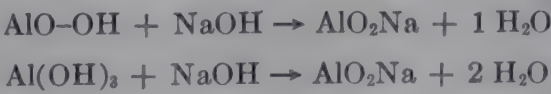
The reaction vessels are clad with lead. (See also Fluorine compounds, inorganic.)

The Manufacture of Alumina

As previously stated, all the alumina produced in the world, with one or two exceptions only, is extracted from bauxite, wherein it exists in its hydrated form. Manufacture consists, therefore, of separating the alumina from the various impurities of the bauxite, a process accomplished entirely by chemical means. For this purpose, advantage is taken of the amphoteric properties of the aluminum ion, which permit the metal to be solubilized in the form of an alkaline aluminate, particularly the sodium aluminate.

The first such process, used in France from 1865 on, was that of Sainte-Claire Deville. The sodium aluminate was prepared by calcining the bauxite with sodium carbonate at 1100°C; the calcined material was then washed with alkali, giving sodium aluminate solution, from which the alumina was precipitated by carbon dioxide. After 1895, parallel with the development of the electrolytic process for aluminum, the above method gradually gave way to that devised by the Austrian chemist Bayer, which is the one almost universally used nowadays. However, the principles of the Sainte-Claire Deville process are still being employed today, especially for treating certain siliceous bauxites and nephelines.

The Bayer process is carried out entirely in the aqueous phase, taking advantage of the solubility equilibria of the alumina hydrates in the caustic soda solution, in accordance with one or the other of the following equations:



These solubilities depend on the caustic soda concentration and on the temperature. As the reactions are endothermic in the direction of solution, an increase in temperature increases solubility. Hence a closed circulation of caustic soda solution is employed, in which the following operations may be performed in turn: (1) Solution of the alumina, at a high temperature and by the use of a high caustic soda concentration; (2) separation of the insoluble impurities of bauxite (red muds) and their washing in order to recover the caustic soda; (3) partial precipitation of the alumina trihydrate at a lower concentration of caustic soda and at a lower temperature; (4) regeneration of the solutions necessary for dissolving the alumina by evaporation of the water introduced for the washings; (5) finally, transformation of the trihydrate to anhydrous alumina by calcination at 1200°C .

Figure 1 shows the principles of the Bayer process. The various operations are described below.

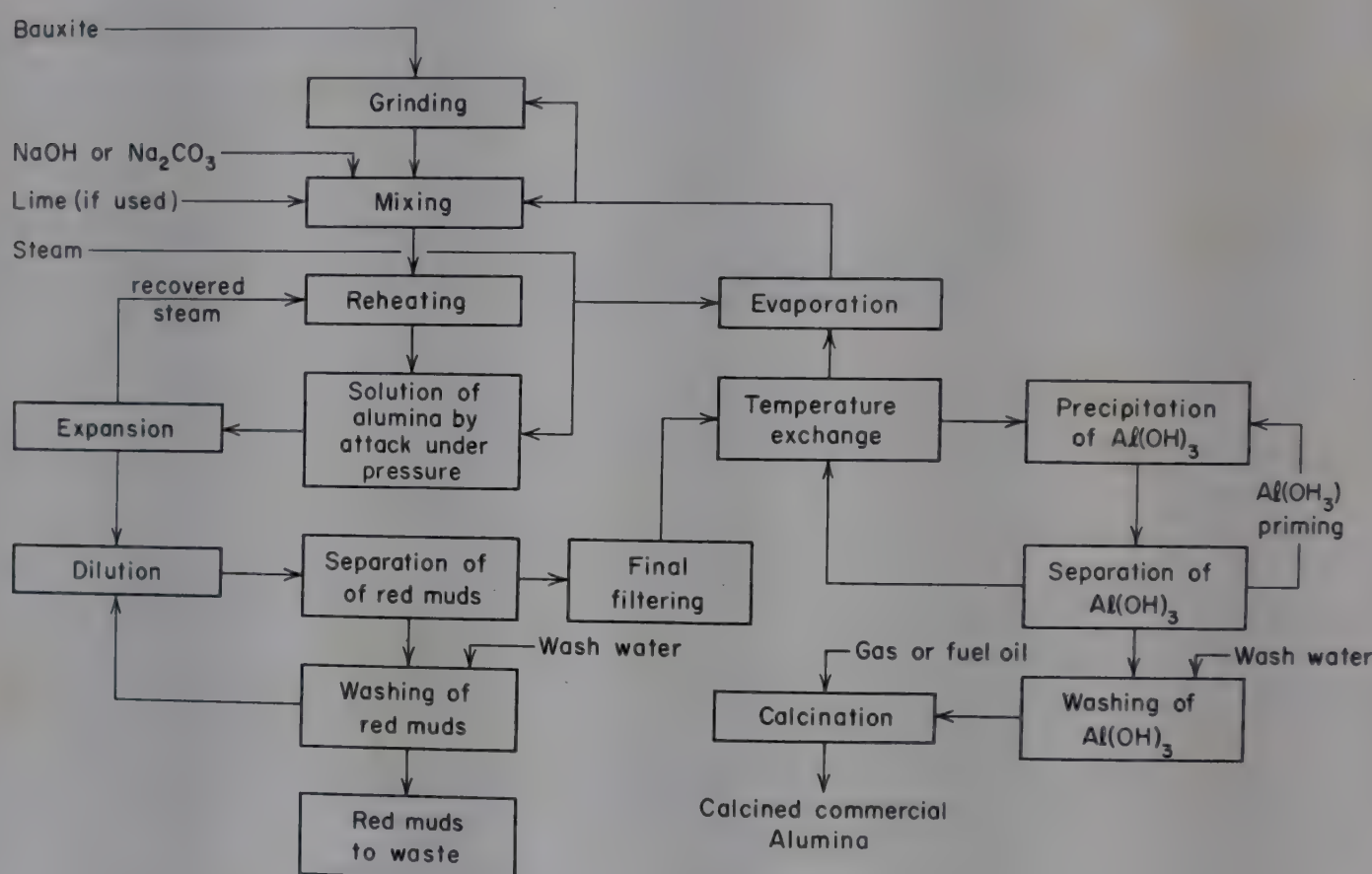


Fig. 1. Diagram of the Bayer process.

SOLUTION OF THE ALUMINA—ATTACK ON THE BAUXITES

The trihydrate of alumina (gibbsite or hydrargillite) is more soluble than the monohydrates (boehmite and diaspore). Therefore, two types of treatment have evolved, as follows:

1. The European type, where it has been necessary to use heavy concentrations of caustic soda (200 to 300 g of Na₂O per liter) at high temperatures (from 200 to 250°C , corresponding to pressures of 35 kg/cm² (ca 500 psi) and higher), in order to deal with the European bauxites containing boehmite.

2. The American type, where in order to deal with the trihydrated tropical bauxites it is sufficient to use caustic soda solutions containing from 100 to 150 g Na₂O per liter at temperatures between 120 and 140°C . However, the recent utiliza-

tion in the Americas of bauxites which contain a certain proportion of boehmite, such as those which are found in Jamaica, actually necessitates the use of high-pressure treatment.

This attacking of the bauxite is carried out continuously in a series of steam-heated autoclaves, into which the ground bauxite suspended in the sodium aluminate lye is injected by pumping. Connected therewith is equipment for recovering much of the heat by interchanges between the lye entering the treatment vessel and that leaving it, usually through the intermediary of the vapor produced by cooling of the hot liquids.

As diasporite is more difficult to dissolve in caustic soda than are other bauxites, it was thought, until recently, that this type could not be treated by the Bayer process; but now, by the use of still higher temperatures (250°C and above) and of certain special devices, diasporite also can be broken down in the aqueous phase.

SEPARATION AND WASHING OF THE RESIDUES

The insoluble residues remaining after the attack are commonly known as red muds. They embody the iron oxides from the bauxite as well as some sodium aluminosilicate, which is an insoluble ternary compound produced by transformation during the attack upon the aluminum silicate (kaolinite) of the bauxite; some titanium oxide (TiO₂) and various other secondary impurities of bauxite are also present.

Generally these muds appear as very fine particles (sometimes less than a micron in size) which are difficult to separate and wash. These operations are usually performed by continuous decanting and by the washing of successive solutions and decantations, countercurrently. The lyes from the washing, which have a low caustic soda concentration, are added to the lyes that were used for the attack; this dilution facilitates decanting of the muds, which is done at about 100°C, and also aids in the final precipitation of alumina. For the usual bauxites rich in Fe₂O₃ the quantity of muds to be washed is very large, amounting to 1000 kg or more for each 1000 kg of alumina, so that these operations call for very large facilities for continuous decanting or thickening. In exceptional cases, in the treatment of certain high-quality bauxites such as those from Guiana which furnish a small amount of mud, the separation and washing can be done by filtration.

PRECIPITATION OF THE HYDRATED ALUMINA

After a final filtration, designed to eliminate the last traces of insoluble mud, "aluminate liquors" very rich in alumina are obtained, which exhibit a molecular ratio of roughly 1.5 to 1.8:1 for Na₂O/Al₂O₃. These liquors are cooled by exchange down to between 50 and 60°C, and are then ready to precipitate about 50% of their alumina content. This precipitation is the reaction previously shown, carried from right to left, and is in fact a hydrolysis of the sodium aluminate or, more correctly, of the ions AlO₂⁻ or Al(OH)₄⁻, which are assumed to exist in the solutions of sodium aluminate. As this reaction is carried out at approximately 50°C, it yields exclusively the alumina trihydrate (hydrargillite), which is the stable solid phase at this temperature.



But the aluminate liquors are metastable at this temperature, so that the reaction is slow and has to be primed. Furthermore, if due caution is not exercised, the

precipitation yields an alumina so fine as to resemble a gel, which can neither be filtered nor washed. Therefore, in order to carry out the precipitation on an industrial scale the aluminate liquor is seeded by adding some precipitated trihydrate and the mixture is stirred; the seeding thus serves to support the precipitating hydrate and makes it settle in the form of small agglomerates of well-crystallized hydrargillite, varying from 5 to 100 microns in diameter, which are easy to separate and wash. The precipitation must be carried out under carefully controlled conditions of concentration and temperature, as these factors determine the texture of the product. As the reaction is slow and limited, it takes 50 to 80 hours to obtain the desired degree of precipitation. Hence, agitating tanks of large volume play a very important part in any alumina-producing installation. In Europe this precipitation is commonly called decomposition; it is the essential characteristic of the Bayer process. (See also Aluminates under Aluminum compounds.)

EVAPORATION

As the circulating aluminate solution has been diluted, prior to precipitation, by the water used to wash the muds, the excess water is evaporated in multiple-stage equipment of the classical type in order to restore the concentration required for attacking the mineral.

CALCINATION

The hydrated alumina is separated and washed by filtration, usually in rotary filters. These filters feed large rotary furnaces, similar to cement kilns, wherein the alumina is calcined at about 1200°C. This operation is necessary not only for the purpose of eliminating the 45% of water (which includes the 30% combined water present in the hydrated material), but also for giving some of the alumina the crystalline α (or corundum) form, which is the most advantageous for the electrolysis.

Calcined technical alumina for aluminum production is thus obtained in the form of a white powder consisting of aggregates which range in size from a few up to about 100 microns and which are made up of monocrystals of anhydrous alumina at various stages of crystallization.

The physical properties of this alumina, characterized by its particle size and degree of calcination, are important to the user. One such property is its content of residual combined water and of adsorbed water. Furthermore, the alumina should be as pure as possible. An alumina of good quality has the characteristics shown in Table 7.

Table 7. Composition of a Good Alumina

Composition	Percent
H ₂ O, combined (loss on calcination)	0.05 to 0.15
H ₂ O, adsorbed (loss at 110°C)	0.20 to 0.50
SiO ₂	0.005 to 0.015
Fe ₂ O ₃	0.005 to 0.020
TiO ₂	0.004 to 0.005
P ₂ O ₅	<0.002
V ₂ O ₅	<0.001
ZnO	<0.010
Na ₂ O	0.40 to 0.80

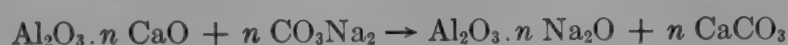
The only impurity of which any appreciable amount remains is the sodium included in the crystalline lattice, and it does not interfere with the electrolysis.

OTHER PROCESSES

In the treatment of highly siliceous bauxites, the Bayer process is supplemented by a feature derived from the Sainte-Claire Deville process. The red muds, which are very rich in sodium aluminosilicate, accordingly undergo calcining at 1100 to 1200°C after addition of calcium carbonate and a complement of sodium carbonate. The greater part of the silica thereupon changes to a dicalcium silicate and the alumina changes to sodium aluminate, which is washed in a lye and restored to the Bayer production circuit. This *combination process*, or *sinter process*, as it is also called, is used in the two alumina factories treating the bauxites of Arkansas.

For some years past a similar technique has been applied on a large scale in the U.S.S.R. for making use of the nephelines mentioned previously, though without the Bayer "attack." Calcining the nepheline and calcium carbonate mixture likewise yields dicalcium silicate and alkaline aluminates, from which the alumina is precipitated by carbon dioxide, whereby sodium carbonate and potassium carbonate, which can be recovered, are obtained. The calcium silicate muds are reheated to produce cement. As the nephelines are poor in alumina (around 20%) and rich in silica, the resulting quantities of cement are very large so that cement and alkaline carbonates as by-products play a predominant part in the economics of the process.

Other processes using calcium aluminate have been proposed and tried. By calcination or fusion of the aluminous ore with limestone, a clinker or slag is obtained which consists of mixed calcium silicates and aluminates. The alumina is then solubilized by addition of a sodium carbonate solution, according to the equation



after which it is precipitated by carbon and yields sodium carbonate, which is restored to the circuit.

The only installation of this type of process which has survived is a small Norwegian works, dating from 1936, which uses the Pedersen technique. In this operation, the calcium aluminate slag is obtained from an electric furnace producing cast iron as a by-product.

For fifty years, all over the world, many laboratory and even pilot-plant investigations have been undertaken with a view to extracting alumina from clay by the adoption of various basic or acid processes. Technically several of these processes are possible, but economically they are not viable as long as the world still has access to reserves of bauxites. (See also Aluminum sulfate under Aluminum compounds.)

Electrolysis of Alumina

The underlying principle consists in decomposing alumina by means of a continuous current which flows through an electrolytic cell containing alumina (Al_2O_3) dissolved in molten cryolite (Na_3AlF_6). The metal is deposited at the cathode whereas the oxygen passes to the anode. As the operation is carried out between 940 and 980°C, a large fraction of the electrical energy is needed to maintain the electrolyte in a molten condition by means of the Joule effect.

The mechanism of the process whereby aluminum is electrolyzed is actually still understood imperfectly. An initial theory is based on the ionization of alumina.

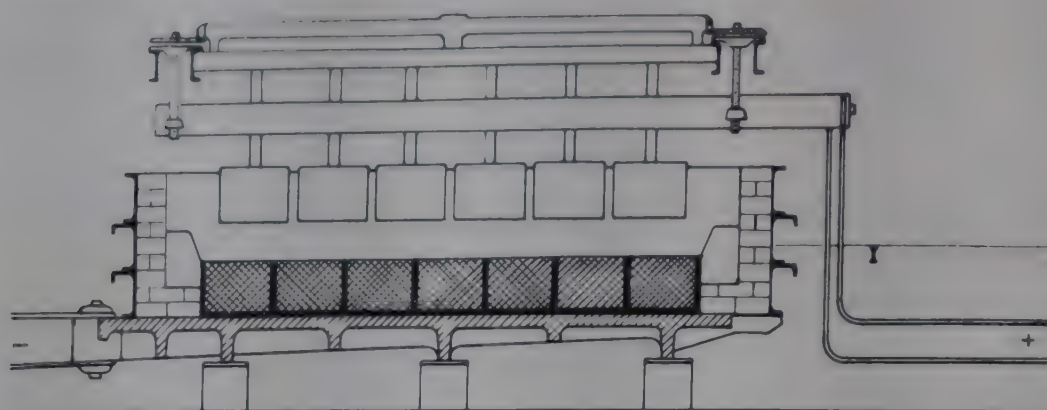


Fig. 2. Bath for electrolyzing aluminum with prebaked anode.

According to this theory the cation Al^{3+} discharges directly at the cathode and the anion O^{2-} , at the anode, where it forms carbon dioxide by combining with the carbon of the anode. By a secondary reaction with small particles of the aluminum or sodium and with the carbon, part of the carbon dioxide is transformed to carbon monoxide.

According to another theory, the sodium fluoride (NaF) is ionized. The cation Na^+ , discharged at the cathode, reacts with the aluminum fluoride (AlF_3) of the bath to form aluminum. The anion F^- , discharged at the anode, decomposes the alumina, yielding AlF_3 and oxygen. The oxygen then reacts with the carbon of the anode as it does according to the first theory (3,4).

The electrolytic cell is essentially comprised of a rectangular steel tank, which is lined with refractory insulating bricks and with an inner lining of baked carbon (see Carbon (baked and graphitized)), since carbon is the only material able to withstand the corrosive action of the molten fluorides.

The carbon blocks at the bottom are joined by steel bars sealed into them by cast iron and these blocks are the ones that form the cathode. In this sense the entire assembly constitutes the cathode, but in fact the true cathode is the molten aluminum deposited there in the course of the electrolysis.

There are two types of anode, as follows:

1. Prebaked anodes are rectangular blocks of very pure carbon obtained from petroleum coke or pitch coke (with an ash content of less than 0.5%). Modern cells, rated at 50,000 to 100,000 amp, ordinarily have the following dimensions: Length, 90 cm; width, 40 cm; height, 50 cm. These anodes are suspended in the electrolyte as shown in Figure 2. Their resistivity ranges from 5000 to 6000 microhm-cm. The current density at the anode lies between 1 and 1.3 amp/cm².

2. The Söderberg continuous and self-baking anode is formed by a paste of pure carbon and pitch which has been filled into a rectangular steel mold. The baked portion is suspended above the cell at a height which can be regulated by means of screw jacks. The lower portion of the anode is heated to about 950°C when dipped into the electrolyte. The continuous current is led to the anode by vertical or inclined steel bars known as pins or stubs. The resistivity of the Söderberg anode is about 30% higher than that of the prebaked anode; the current density is lower, ranging from 0.7 to 0.9 amp/cm². In modern 100,000-amp cells (Fig. 3) the Söderberg anode is 6.5 m long, 2 m wide, and 1 m high, weighing up to 20 tons.

Large modern plants are equipped with cells operating at 100,000 amp at a voltage drop of 4.5 volts. Experiments for the purpose of using still higher currents of up to 150,000 amp are in process. Germanium or silicon rectifiers are used at

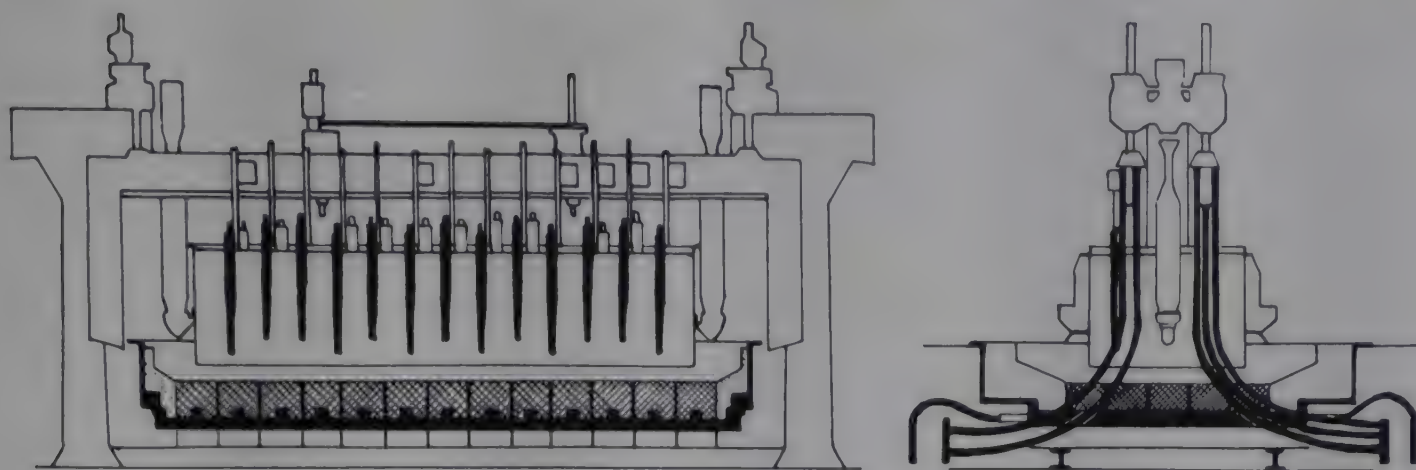


Fig. 3. Bath for electrolyzing aluminum with Söderberg electrode.

Péchiney to obtain the continuous current, by conversion (more than 97% efficient) from a three-phase alternating current. In the United States these rectifiers are beginning to be employed but most of the installed capacity uses mercury vapor Ignitrons.

The electrolyte in industrial use has essentially four constituents: cryolite, 80–85%, calcium fluoride, 5–7%; aluminum fluoride, 5–7%; alumina, 2–8%.

The melting point of the cryolite is 1006°C. Experience has shown that an addition of 1% by weight of any of the three bath additives lowers the melting point by 4 to 5°C.

The density of the molten bath at 950°C is approximately 2.1 g/ml and that of aluminum at the same temperature is 2.3 g/ml. The aluminum, being heavier, thus settles at the bottom of the bath.

The aluminum fluoride exerts a considerable influence on the current efficiency as it lessens the solubility of aluminum in the bath; it consequently reduces the losses of metal by secondary reaction with the carbon formed at the anode.

The electrical characteristics of the electrolysis, in cells operating at 100,000 amp, are as follows:

potential across the terminals of the cell	4.5 volts
decomposition potential of the alumina	1.7 volts
current density in the bath	0.7 amp/cm ²
distance between electrodes	5 cm
resistivity of the bath at 950°C	0.50 ohm-cm

The electrochemical work performed in decomposing the alumina corresponds to 1.7 volts.

According to Faraday's Law, taking account of the atomic mass of the aluminum (which is 26.9815) and of its valence, 3.9 g of aluminum are theoretically deposited by 1 Faraday unit or 26.8 ah (ampere-hour). In practice, the average Faraday efficiency for 100,000-amp cells is 90%.

If V stands for the voltage across the terminals of the cell, I for the current in amperes, e for the decomposition voltage of the alumina, ρ for the Faraday efficiency, R for the total ohmic resistance of the bath, then the total power VI supplied to the bath is divided between a nonheating power represented by eI , and a heating component which includes the following two terms:

$$(1 - \rho)eI \text{ and } RI^2$$

$$VI = \rho eI + (1 - \rho)eI + RI^2$$

The energy efficiency of the bath can be written as $\rho e/V$ and, in the case of a 100,000-amp bath, the efficiency is given by $(0.9 \times 1.7)/4.5 = 0.34$, or 34%.

Actually this figure has to be corrected by adding a constant, 0.04 (4%), in order to allow for the heating of the raw materials, particularly of the alumina. The energy efficiency, therefore, is 38%, which means that 62% of the energy supplied to the cell is dissipated in heat.

In a modern cell, the manufacture of one ton of alumina consumes

1,890 kg	of alumina
450 kg	of anodic material
70 kg	of cryolite, and
15,000 kw-hr	of energy

A good portion of the metallic impurities present in the raw materials, especially Fe, Si, Ti, V, and Mn, may also be found in the aluminum. That is why the raw materials should be prepared in as pure a state as possible. As a rule, the metal is 99.6 to 99.8% pure.

The operation of such cells calls for great care, especially in the composition of the bath and in the adjustment of the electrical conditions, in order to attain maximum yields and a steady, optimum operating temperature which experience has shown to be fixed at $960 \pm 10^\circ\text{C}$. A constant temperature may advantageously be obtained by allowing a layer of the bath to solidify on the surrounding carbon lining. This affords protection and, at the same time, serves to regulate the temperature.

The alumina is the only constituent of the bath which, at least in theory, disappears completely. When the alumina content has dropped to about 2%, the potential across the terminals of the cell suddenly rises to 30 to 50 volts. This phenomenon is called the anode effect. It is suppressed by charging the bath with alumina so as to raise the concentration once more to approximately 8%.

The removal of the metal from modern cells is accomplished by siphoning under a vacuum. As a rule this is done every two days, and sometimes every day.

Electrolysis gives rise to mixed gases formed by the discharge of oxygen from the alumina at the carbon anode. The gases sampled from the middle of the cell, where there is no contact with air, contain approximately 75% carbon dioxide and 25% carbon monoxide. The latter component burns as it is released but the gases also carry with them hydrogen fluoride and other volatile fluorides and, in the case of a Söderberg anode, hydrocarbons.

To avoid air pollution, the gases must be rid of the fluorine compounds. This is why modern plants possess very effective equipment for collecting these harmful constituents, including (in succession) electrostatic precipitators and scrubbing towers sprayed with a sodium carbonate solution. A large part of the fluorine consumed can thus be recovered.

Other Processes for Obtaining Aluminum

The traditional process for manufacturing aluminum has disadvantages which affect its selling price, in that (1) the power consumption of even the largest electrolytic reducing cells does not exceed 500 kw; (2) a low-voltage direct current has to be used; and (3) the chemical plants in which the preliminary purification of bauxite is carried out require a heavy capital investment.

Attempts have, therefore, been made to obtain aluminum by the reduction of aluminous minerals in electric arc furnaces resembling those used for manufacturing calcium carbide or ferrous alloys. This method, however, also has its disadvantages, in that (1) the materials have to be heated to about 2000°C (as against 1000°C in electrolysis) and (2) the theoretical consumption of the reducing carbon is greater, because the gases escape in the form of carbon monoxide (whereas the gases evolved in electrolysis contain principally carbon dioxide).

Furthermore, at so high a temperature pure aluminum cannot be obtained directly because the metal is far too volatile. This involves allowing elements such as iron and silicon to be present which, by alloying themselves with the aluminum, lower its vapor pressure. Starting from bauxite, kaolin, or cyanite it is thus fairly easy to use an arc furnace for obtaining alloys containing 60 or even 70% of aluminum, the remainder being mainly iron and silicon in proportions varying according to the minerals used. A second stage is then necessary in order to refine these alloys and to obtain the pure aluminum (5).

On the subject of these alloys it should also be noted that silicon requires more energy for its reduction than iron. In addition, silicon recovered in a very impure state in the residue from refining is difficult to sell. But the iron, too, has its disadvantages, in that the compound FeAl_3 is very stable and is not decomposed in many of the refining processes that will be mentioned. As a result, the efficiency of extracting aluminum remains low if a considerable amount of iron is present.

Many processes have been devised for refining the alloys produced in arc furnaces. These processes can, of course, also be applied to obtaining pure aluminum out of scrap from alloys used in the secondary aluminum industries. Some processes even make it possible to obtain aluminum purer than that from electrolytic reduction cells.

In the first group of these processes the aluminum is extracted from the alloy by electrolytic refining in a bath of aluminum chloride at 180°C, or in an organic bath at approximately room temperature. But none of these procedures has reached the industrial stage.

In a second group of processes the alloy is brought into contact with a liquid metal more volatile than aluminum, such as magnesium, zinc, or mercury. Only the aluminum is dissolved. After filtration to eliminate the residue, the volatile metal is distilled and pure aluminum remains. These methods do not destroy the compound FeAl_3 . The magnesium process was employed in Germany during the last war for treating airplane scrap. The zinc process, which is especially suitable for the manufacture of Silumin (13% silicon), was developed in France in a pilot plant which turned out one ton a day up to 1952. The mercury process, by which it is possible to obtain aluminum 99.995% pure, is still being studied.

A third group of processes takes advantage of the fact that aluminum becomes monovalent at high temperatures. Thus, by bringing vapors of aluminum fluoride or aluminum chloride into contact with the alloy at about 1000°C, the following reactions occur:



The vapors of AlF or AlCl are then conveyed to a slightly colder zone where the inverse reaction takes place, resulting in the condensation of very pure aluminum.

These processes are applicable even where the starting materials are alloys fairly rich in iron.

British and Canadian aluminum manufacturers have given much attention to the chloride process. To get rid of certain impurities, such as for instance manganese, which are apt to be carried away with the AlCl_3 , this latter vapor is purified by being brought into contact with a certain amount of liquid aluminum extracted from the already condensed metal. Extremely pure aluminum can apparently be obtained in this way. A pilot plant is under construction in Canada.

A fourth group of processes starts not from an alloy of the aforementioned type but from pure alumina. This involves thermal reduction by carbon either in the presence of an excess of carbon (known as the carbide process) or in the presence of nitrogen (known as the nitride process). According to circumstances, the pure alumina which serves as the starting point may be either alumina obtained by the traditional Bayer method or natural corundum or alumina from any other source. This freedom to choose between several kinds of alumina permits adapting an operation to varied economic conditions.

The *carbide process* consists in the use of an arc furnace to manufacture an $\text{Al}-\text{Al}_4\text{C}_3$ alloy that may contain up to 80% of uncombined aluminum. This operation is performed at about 2400°C so that the alloy is fluid enough to flow out of the furnace easily. On cooling, the aluminum carbide crystallizes in a lattice whose interstices are filled with pure aluminum, and if the cooling is sufficiently slow, these interstices are large. The larger they are, the easier is it to separate the aluminum by leaching the alloy with molten chlorides. Aluminum obtained in this manner is particularly free from titanium and vanadium. The carbide residue is returned to the arc furnace.

The *nitride process* consists in bringing carbon and nitrogen into contact with alumina at approximately 1750°C , which gives rise to a solid aluminum nitride. This is placed in a vacuum furnace at about 1800°C , where it dissociates into aluminum vapor and nitrogen. The aluminum vapor is condensed in a cooled condenser.

Very Pure Aluminum by Electrolytic Refining

The Hall-Héroult process cannot ensure a purity higher than about 99.90%. Other techniques were therefore required when an extremely high purity was desired.

The principle of electrolytic refining, as described by Betts in 1905, is still in use today. It is based on the use of a bath containing three layers. The bottom of the cell, which is a carbon anode, as well as its sides which are nonconductors of electricity, are covered with a dense layer of aluminum-copper alloy. Upon this layer rests another layer of electrolyte which contains aluminum cations. The density of this layer is slightly below that of the aluminum-copper alloy but above that of aluminum itself. Finally, covering these is a third layer which is pure refined aluminum serving as the cathode.

In 1924 Hoopes, of the Aluminum Company of America (Alcoa), revived the idea of electrolytic refining in three layers. The anodic layer is an aluminum-copper alloy containing 25% of copper. The electrolyte is a mixture containing 60% of cryolite, 40% of barium fluoride (BaF_2), and from 1 to 3% of alumina. Graphite electrodes are used so that the current has to leave through the cathodic layer of refined aluminum. The nonconducting walls are formed of a solidified portion of the bath. Alcoa built such a cell which operated at 950 to 1000°C , with 20,000 amp and at 5 to 7 v. The metal it produced was generally no purer than 99.98%.

In 1932 the P  chiney Company in France perfected a three-layer refining process which was, and still is, very successful industrially. Here again, the anodic alloy is a binary Al.Cu alloy having a composition close to the eutectic (which contains 33% copper). The electrolyte is a chloride-fluoride bath containing 60% of barium chloride (BaCl_2) and 40% of chiolite, $\text{AlF}_3 \cdot 1.5\text{NaF}$ (a synthetic salt produced very much like synthetic cryolite). The melting point of the bath is 720°C and the resistivity is 0.7 ohm-cm. The nonconducting walls are of magnesia brick. The cathodic current connection is obtained through graphite electrodes. These cells operate with 20,000 amp at 6 volts, and at 750°C , a temperature at which the three layers have densities approximating 3.1, 2.7, and 2.4 g/cm^3 , respectively. Whereas the anodic Faraday efficiency is 100%, the cathodic efficiency—reduced by the inevitable losses—is 98%. The metal may attain a purity of 99.995%.

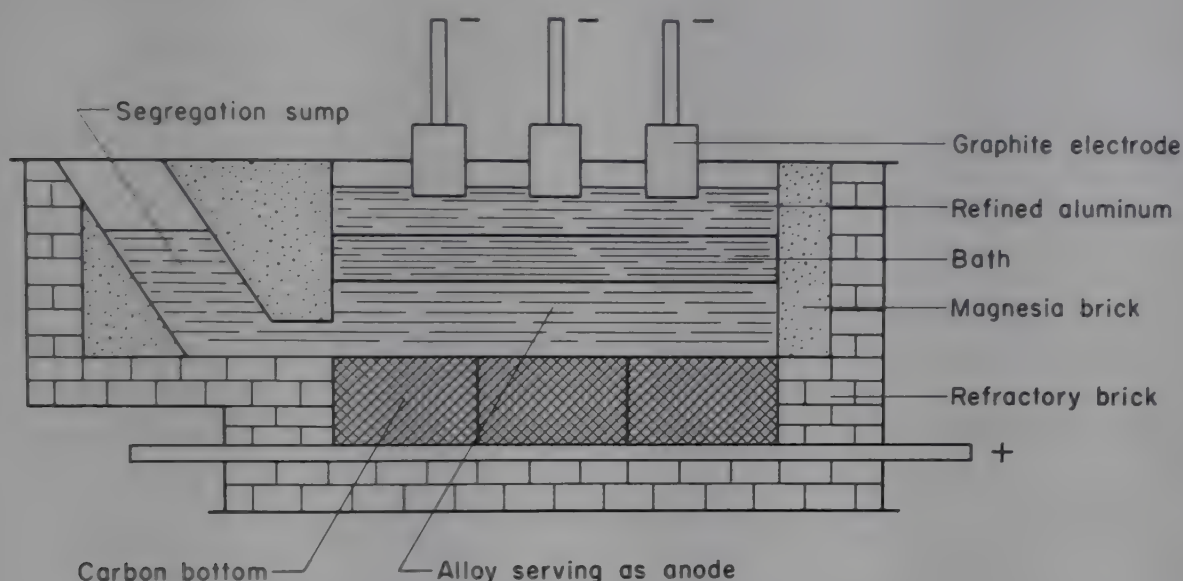
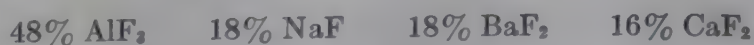


Fig. 4. Bath for the electrolytic refining of aluminum (P  chiney system).

The cell (Fig. 4) possesses an important new feature which makes a continuous industrial operation possible, namely, a lateral sump that communicates with the anodic layer. This serves at the same time to supply this layer with the liquid aluminum to be refined—as a rule, virgin metal of 99.6% purity—and to withdraw impurities, such as Fe and Si, which are more electropositive than the aluminum. These impurities collect in the anodic layer. When Fe and Si exceed 7%, they are withdrawn in the form of a solidified, crystalline alloy, having an average composition of 12% Fe, 7% Si, 22% Cu, and 55% Al (6).

The pouring of the refined aluminum is done by means of pure graphite equipment, at, for instance, two-day intervals. In the production of each ton of refined aluminum, 18,000 kw-hr, 60 kg of bath material, and 20 kg of graphite is consumed.

In 1937, the Soci  t   Suisse de l'Aluminium Industrie at Neuhausen patented a three-layer refining process based on the use of a bath consisting exclusively of fluoride compounds having the following composition:



The design and operating conditions of this bath are those of the P  chiney process. Similar processes, in which either an all-fluoride bath or a fluoride-chloride bath is used, are in operation in the U.S.

Properties of Aluminum

The physical characteristics shown below are given for very pure aluminum (99.99%). The reactions of aluminum are shown under Chemical properties (p. 949). The usual impurities found in aluminum are discussed under Composition of aluminum (p. 954).

PHYSICAL PROPERTIES

atomic number	13	electronic structure	3s ² , 3p ¹
atomic mass	26.9815 (¹² C = 12.000)	capture cross-section for thermal neutrons, barns/atom	0.215
crystalline form, at 25°C	face-centered cubic (a = 4.04958 ±0.000025 Å)	mp, °C	660.1
		bp (760 mm), °C	2327
sp gr at 20°C, g/cm ³	2.699	heat of fusion, cal/g	94.6

Table 8. Specific Heat

°C	cal/(g)(°C)	°C	cal/(g)(°C)
-240	0.0092	200	0.232
-173	0.112	300	0.241
-123	0.168	400	0.249
-23	0.204	500	0.264
0	0.209	600	0.280
20	0.214	0-658	
100	0.223	(average value)	0.25

Table 9. Coefficient of Linear Expansion

°C	per °C ^a	°C	per °C ^a
20	22.4	20-300 ^b	25.4
100	23.5	20-400 ^b	26.5
300	28.4	20-500 ^b	27.7
500	31.1	20-600 ^b	28.7
20-100 ^b	23.8	16-191 ^b	18.3
20-200 ^b	24.6		

^a All values in this column are to be multiplied by 10⁻⁶.

^b Average values shown for the given spread in temperature.

Table 10. Thermal Conductivity

°C	kcal/(sec)(cm ²)(°C/cm)	°C	kcal/(sec)(cm ²)(°C/cm)
-250	0.37	200	0.52
0	0.48	400	0.55
20	0.50		

For reflecting power, see Figure 5. Absorbing power and emissive power vary within fairly wide limits, according to surface conditions (8). (See Table 11.)

Table 11. Absorptive Power and Emissive Power of Aluminum

Surface characteristics	Absorbing power for solar light, %	Emissive power to surrounding medium, %
bright aluminum (as rolled)	14	<10
anodized aluminum, thickness of film, μ		
0.9	15	ca 40
1.5	15	60
3	15	75
6	15	>90
alloy composed of aluminum anodized with 4% silicon, thickness of film, μ		
10	60	>90

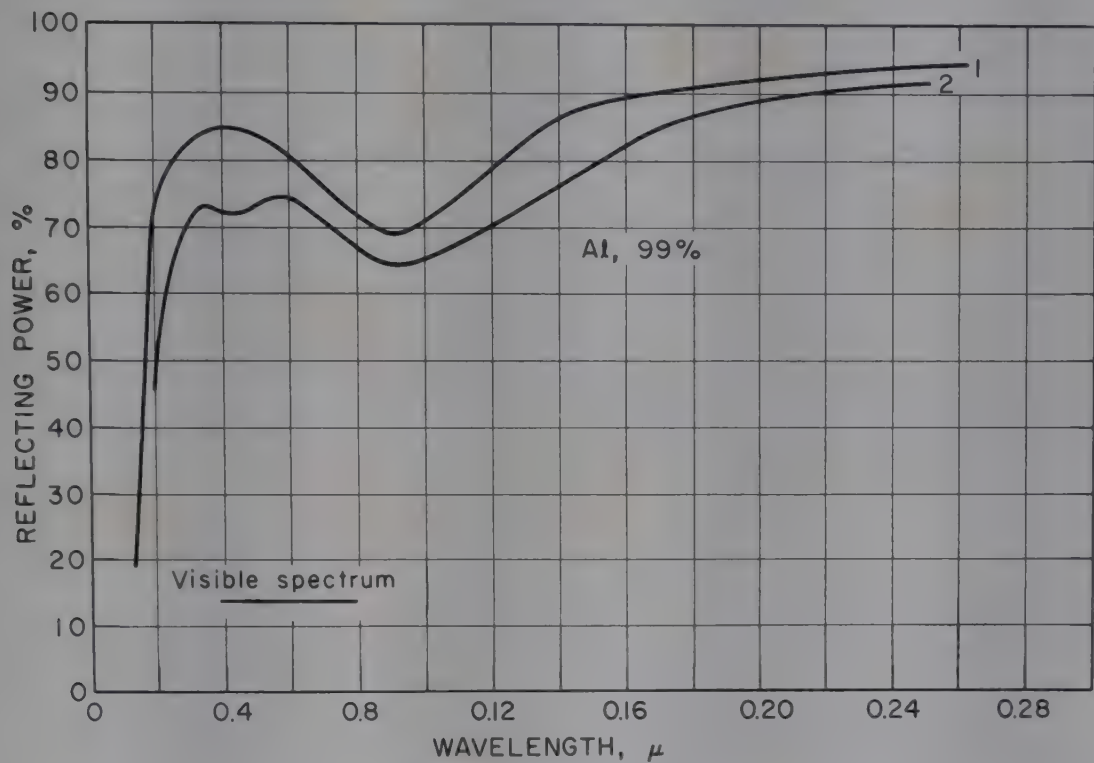


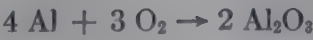
Fig. 5. Reflecting power of pure aluminum as a function of wavelength. 1, Anodized; 2, polished. (From Schenck (7).)

It may thus be seen that, given the right type of surface, aluminum makes an excellent reflector (especially for ultraviolet); it may also be used as a selective cold or hot wall or as a body approximating the effect of a black body.

Additional data are as follows: electrical resistivity, 2.655 microhm-cm; temperature coefficient of the electrical resistivity, 0.0043/ °C; magnetic susceptibility, 0.6×10^{-6} cgs units. Aluminum becomes superconductive at the transition temperature 1.4°K.

CHEMICAL PROPERTIES

Reactions with Elements and Inorganic Compounds. Aluminum reacts with oxygen according to the equation



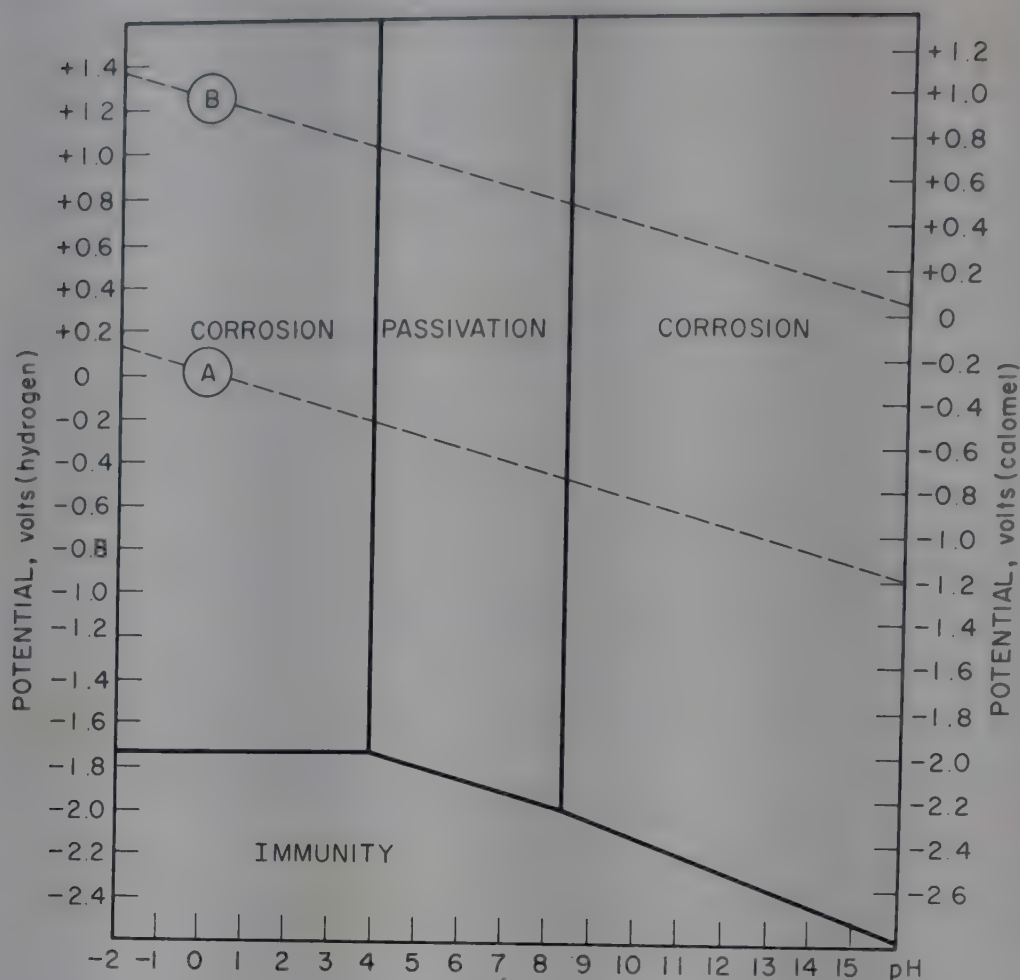


Fig. 6. Voltage-pH chart for aluminum. Theoretical conditions for corrosion, immunity, and passivation of Al at 25°C based on assuming passivation by a boehmite ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$) film and taking a solubility of 10^{-4} gram-atoms of Al per liter of solution to be the limits of corrosion. The lines A and B represent the stability limits of water.

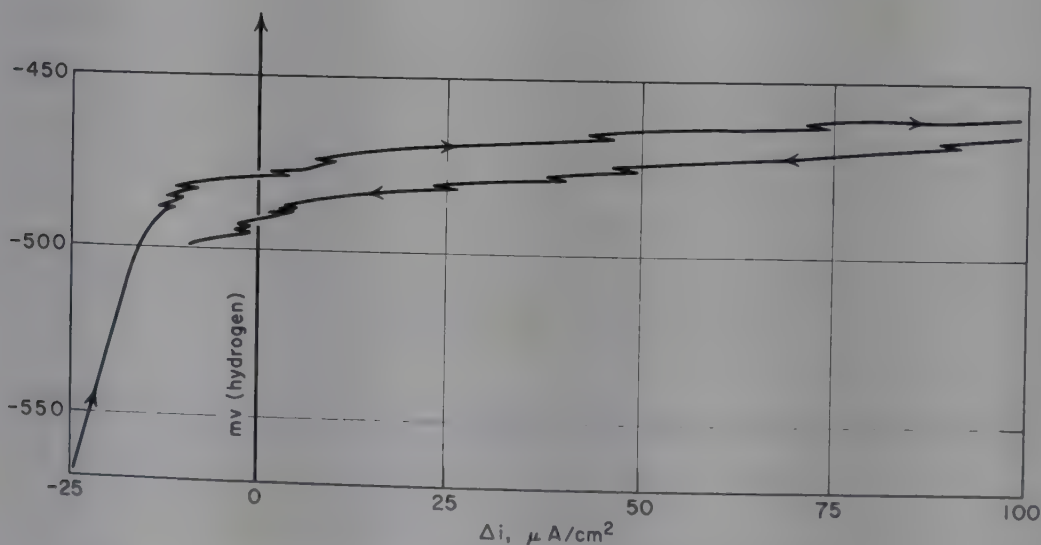


Fig. 7. Polarization curve for aluminum in artificial sea water.

Its heat of formation with oxygen is very high, viz, 7390 cal/g, or 199 kcal/atom, and this explains why aluminum is not found in an uncombined state and why it was not produced in the metallic state until the middle of the nineteenth century.

The oxide which is formed covers the metal with a film and prevents the reaction from continuing. The thickness of this film at room temperature is between 0.001 and 0.1 micron. This deposit enables the metal to maintain its white luster, the

brightness of which increases with the purity of the metal. When hot the deposit is thicker and covers the molten metal with a protective layer.

Aluminum, even as a thin foil, will not burn in air, but as a powder, in a very finely divided state, it oxidizes very violently, with explosion. This is why such a powder is manufactured in an oxygen-deficient atmosphere (4 to 6% O_2) and in the presence of stearic acid (2%) to coat the particles of aluminum.

At relatively low temperatures, the surface film of hydrated alumina which protects the metal is bayerite ($Al_2O_3 \cdot 3H_2O$); above $70^\circ C$, it is boehmite ($Al_2O_3 \cdot H_2O$).

The conditions of passivation for the metal may be inferred from a chart of potential plotted vs pH for the formation of boehmite at $25^\circ C$ (see Fig. 6). The minimum solubility of alumina occurs at pH 5.075; the passivation range lies between pH 4.66 and 6.32. Beyond these limits there is corrosion. This diagram also shows the standard electrode potential for aluminum, which is -1.78 . As this value is so low it follows that aluminum is practically impossible to immunize by cathodic protection in strongly alkaline or acidic environments, where alumina is highly soluble. It can be cathodically protected in nearly neutral solutions (9).

By use of the potentiostatic method for plotting polarization curves, it is possible to predict how aluminum may behave in aqueous solutions (10). Figure 7 shows a polarization curve for 99.5% aluminum in artificial sea water. The corrosion current indicated is fairly high, and increases rapidly with slight increases in the potential (2 v/hr). At the same time the irregularities of the curve show that the corrosion occurs locally rather than uniformly over the surface.

At $180^\circ C$ water rapidly oxidizes pure aluminum and, less rapidly, aluminum of commercial purity. The oxide is formed not only on the surface but also at the boundaries between the grains, leading at first to an increase in the size of the sample and then to its destruction. This effect can be lessened considerably by adding 0.5 to 1% of nickel and iron to the aluminum. It is not advisable to use aluminum alloys above $180^\circ C$ (11).

When small quantities of water or water vapor are present molten aluminum reacts violently, causing an explosion. This is one reason why the molten metal must never be allowed to come into contact with damp tools or containers.

Aluminum at a high temperature also has the effect of reducing many compounds containing oxygen, particularly oxides. Advantage is taken of these reactions in the manufacture of certain metals or master alloys, such as Mn, Cr, ferro-titanium, aluminum-titanium, silico-alumino-titanium, and cupro-titanium, as well as for welding at high temperatures according to a reaction of the following type (Goldschmidt reaction):



Aluminum reduces silica, the silicates, and especially glass. The reaction may start at $600^\circ C$ or between 550 and $700^\circ C$ (depending on the type of glass).

Ozone does not act on aluminum.

Aluminum when hot combines with carbon. Trillat has shown that the reaction between elements in powdered form takes place at $400^\circ C$ but that from the industrial viewpoint melting aluminum along with carbon does not cause any carburization (12). Aluminum carbide, Al_4C_3 , cannot readily be produced except at a high temperature (about $2000^\circ C$). It reacts readily with water, producing methane.

At ordinary temperatures, aluminum is completely resistant both to carbon monoxide and carbon dioxide. At high temperatures, it reacts with carbon monoxide to form Al_4C_3 .

Above 1100°C , aluminum forms a nitride, AlN , which is considered to be an excellent refractory, able to resist very high temperatures.

Hot aluminum also reacts with sulfur to form Al_2S_3 , and with phosphorus to form AlP (stable up to at least 1000°C).

Boron combines with aluminum to give the compounds AlB_2 and AlB_{12} .

Aluminum reacts with the halogens, giving volatile halides (AlCl_3 , AlBr_3 , AlI_3). Aluminum is dissolved by alcohol containing bromine and this property is put to advantage for analyzing alumina in aluminum.

It is disputed whether an aluminum hydride exists, but hydrogen dissolves in aluminum to the extent of 0.3 to 0.5 cm^3 per 100 g of the solid metal. The fused metal, however, can dissolve a greater amount, especially if its temperature is increased. The hydrogen begins to be taken up by the metal even at room temperature in the course of a reaction with water or with an inorganic acid. But molten aluminum becomes charged even more with hydrogen when in contact with steam, and especially in the presence of hydrocarbon combustion products.

Such hydrogen is undesirable as it comes out of solution when the metal solidifies, forming pores in castings. It also appears as blisters on sheets that are being reheated. The hotter the molten aluminum the more hydrogen it takes up, and so the temperature in the furnaces is usually limited to between 750 and 780°C . The methods adopted for getting rid of dissolved hydrogen in molten aluminum consist mainly of keeping the metal covered for some time by a saline flux (such as the eutectic NaCl-KCl) which includes a certain proportion of fluorides (5 to 15% of either sodium fluoride or cryolite or chiolite, $\text{AlF}_3 \cdot 1.5\text{NaF}$) or of bubbling a current of chlorine through the metal.

Inorganic acids behave in different ways. The halogen acids HCl and HF attack aluminum violently. On the other hand, sulfuric acid and nitric acid attack it only slightly, at least in certain concentrations. Phosphoric acid attacks aluminum strongly, but oxides of arsenic are less aggressive. Strong alkalies violently attack aluminum by dissolving the protective layer of alumina. Caustic soda even at 2% concentration is very corrosive. Cement may contain enough free lime to be corrosive.

Ammoniacal solutions, on the other hand, do not attack aluminum.

The halides of the alkali metals and, to a lesser degree, those of the alkaline earth metals are more aggressive in dilute solution than concentrated. Their chlorates and perchlorates have no action on aluminum. Their nitrates and their compounds with sulfur do not, as a rule, cause any attack. Their phosphates may act aggressively on aluminum according to the pH of the solution. Carbonates that are alkaline are always fairly aggressive, but here the action of inhibitors is more marked.

The salts of metals more noble than aluminum do attack it. In particular, aluminum should not be used in contact with mercury and its salts.

Behavior of Aluminum Toward Organic Compounds. Aluminum gives perfect resistance to hydrocarbons, saturated or unsaturated, aliphatic or aromatic, but it should be remembered that traces of alkaline or acid "washings" may be present.

Halogenated derivatives of hydrocarbons have little action on aluminum except for the possibility that the halogen may be liberated, especially where water is also present, leading to the formation of halogen acids. There is a possibility of violent

reaction when finely divided aluminum particles are exposed to certain halogenated hydrocarbons at a high temperature and pressure.

The resistance of aluminum to alcohols is very good, even in methyl alcohol, and it is better still in the higher alcohols. The methods of manufacture and resulting impurities in certain alcohols should, however, be taken into account.

Phenols do not act on aluminum at ordinary temperatures. This is also true of polyhydroxybenzenes and of phenol derivatives having very high molecular weights, even at their boiling points.

Aldehydes, ketones, and quinones are inert to aluminum, and aluminum, in general, does not have catalytic activity, so that aluminum alloys are often used in contact with these substances.

The action of acetic acid is at a maximum for very low concentrations (of the order of 0.02%) and even then it is considered acceptable; it is somewhat more severe at elevated temperatures. With carboxylic acids of higher molecular weight the action on aluminum is still less. Commercial acids may, however, contain impurities which appreciably modify the behavior of the pure substance. Acid anhydrides produce no effect but halogenated organic acids, such as trichloroacetic acid, are very aggressive and cannot be allowed in contact with aluminum.

The amines have basic properties, but this effect becomes less with increasing substitution on the nitrogen and with an increasing number of carbon atoms in the molecule. However, amines may contain impurities from the way in which they are prepared.

Amines may form a protective film on the surface of aluminum. Generally speaking, aluminum is not attacked to any extent when cold but does not resist well when hot. Whereas aniline and its derivatives are generally aggressive, pure ethanolamines have practically no action. Other classes of organic compounds, in general, are inert unless they contain corrosive impurities resulting from their method of manufacture.

Inhibitors. The following may be mentioned among inhibitors that can be used industrially in contact with aluminum or light alloys: Many organic or inorganic colloids (eg, resins, gums, starch, dextrin, sodium silicate, and others); alkaline chromates and bichromates, chromic acid, potassium permanganate, hydrogen peroxide, and other oxidants which tend to reinforce the protective oxide film covering the metal; certain amines, alkaloids, and other nitrogen compounds; certain organic bases, such as ethylamine or aniline, which have the effect of stabilizing halogenated hydrocarbons when a trace of water is present, whereby they prevent the formation of decomposition products which might attack the metal.

Nevertheless, it should be noted that there are no universal inhibitors and that the action of inhibitors is sometimes masked by that of impurities in the materials concerned. The following inhibitors may be mentioned as examples:

Resins are used against very dilute (less than 0.02%) and hot solutions of acetic acid, also against (less than 5%) solutions of hydrochloric acid and formic acid.

Sodium silicate is generally employed to inhibit attack by alkaline substances. From 0.2 to 1% of this material mixed with 5% solutions of sodium carbonate is used to afford protection, for instance, against solutions of alkaline cyanides or against corrosive aqueous solutions containing hydroxides of Na, Ba, Ca, or Li; also against alkaline and alkaline earth hypochlorites, alkaline phosphates, and very dilute solutions (0.2%) of sodium sulfate.

Likewise, potassium dichromate is used to protect aluminum against attack by alkaline liquids, sodium carbonate, and dilute caustic solutions (in the proportion of ten times the weight of the soda content).

Potassium chromate is the usual inhibitor against acidic liquids or neutral salines. A 2% solution is employed against concentrated solutions of calcium chloride, magnesium chloride, or sodium chloride, and a 0.1% solution against 10% nitric acid.

Chromic acid at concentrations of 0.5 to 5% serves to reduce the aggressivity of solutions containing 1 to 2% phosphoric acid up to 100°C.

Among the amines, 0.05 to 0.1% solutions of hexamethylenetetramine deserve mention; they are used in the presence of dilute nitric acid, and triethylamine, to stabilize trichloroethylene.

ALUMINUM AND THE LIVING ORGANISM

From the hygienic point of view, one of the most important characteristics of aluminum is that it has absolutely no effect on life. Thorough experiments have been made by introducing it under the skin or into animal tissues. These experiments have shown that, given proper care to prevent any bacterial infection, the presence of the metal did not produce any discomfort or irritation other than a purely mechanical irritation. Further experiments have shown that aluminum, unlike many other common metals, in no way accelerated the loss of vitamins during cooking. The loss of vitamin C (the most vulnerable vitamin) when milk is pasteurized in an aluminum container does not exceed the (30%) loss incurred when the same operation is carried out in a glass container; but in a copper container, under the same conditions, the vitamin is destroyed completely.

Small quantities of aluminum may be dissolved in certain types of foods, especially those which contain organic acids, such as tomatoes and rhubarb. Beal and others have found that at most 12 mg of aluminum per person might thus be absorbed if all the food had been prepared in aluminum containers, but only 40% of the metal would come from the cooking utensils (13,14). These traces of aluminum salt, which are harmless in any case, do not have any objectionable effect because they are colorless. The product of corrosion in the presence of water is aluminum hydroxide, the very same substance which is prescribed for prolonged and intensive use in the treatment of stomach ulcers.

It has also been shown that the inhalation by animals of aluminum dust simultaneously with silica dust prevents silicosis; the amount of aluminum need be no more than a small percentage of the amount of silica. Repetition of these tests on human subjects shows that the inhalation of fine aluminum dust reduces irritation and dyspnea (difficulty in breathing) in advanced cases of silicosis, but this treatment is still in the experimental stage. Another fact to be weighed is that the application of aluminum foils aids the cicatrization of scars which are slow in healing.

Aluminum and Its Alloys

COMPOSITION OF ALUMINUM

The two main impurities always present in aluminum produced by electrolysis are iron and silicon: Fe, 0.06 to 0.60%; Si, 0.04 to 0.30%.

To this are added certain minor impurities, mainly from the electrolysis bath and from the electrodes. The most important ones are the following (given in ppm):

Ti	40–150	Si	1.5	Cu	20–50
Ga	60–200	V	10–70	Pb	10–100
Mg	20–80	Mn	20–80	Cr	10 (approx)
B	2–5	Zn	100–400	Ni	10 (approx)

The quality of the aluminum is often indicated by a grade, expressed as % pure aluminum (viz, 100% minus % total impurities), the impurities having been determined by the standards of the country concerned. Usually, the impurities are Fe, Si, Cu, and Zn.

Aluminum refined by double electrolysis (and still more that obtained by zone refining) contains considerably smaller amounts of impurities than does aluminum from other sources. In some instances, these impurities may amount to no more than a few parts per million of Fe, Si, Cu, and Mg. In the case of such small quantities, the conventional analyses, by colorimetry or spectrography, are subject to relatively high errors. Radiochemical methods are, therefore, being used after activating the sample by exposure to radiation in experimental nuclear reactors (15). The purity of the metal may also be estimated by measuring its resistivity at a very low temperature (in liquid helium) as this resistivity increases very rapidly with the amount of impurities (16).

ALLOYS OF ALUMINUM

Only the principal phase diagrams have been reproduced below (17–20).

Binary Alloys. In the diagrams Al–M, the α phase is the solution of the metal M in aluminum. In the case of, eg, the Al–Fe diagram, at the eutectic temperature, the α phase may contain up to 0.03% Fe; in the case of the Al–Si diagram, up to 1.65% Si. But there is no transformation of the aluminum.

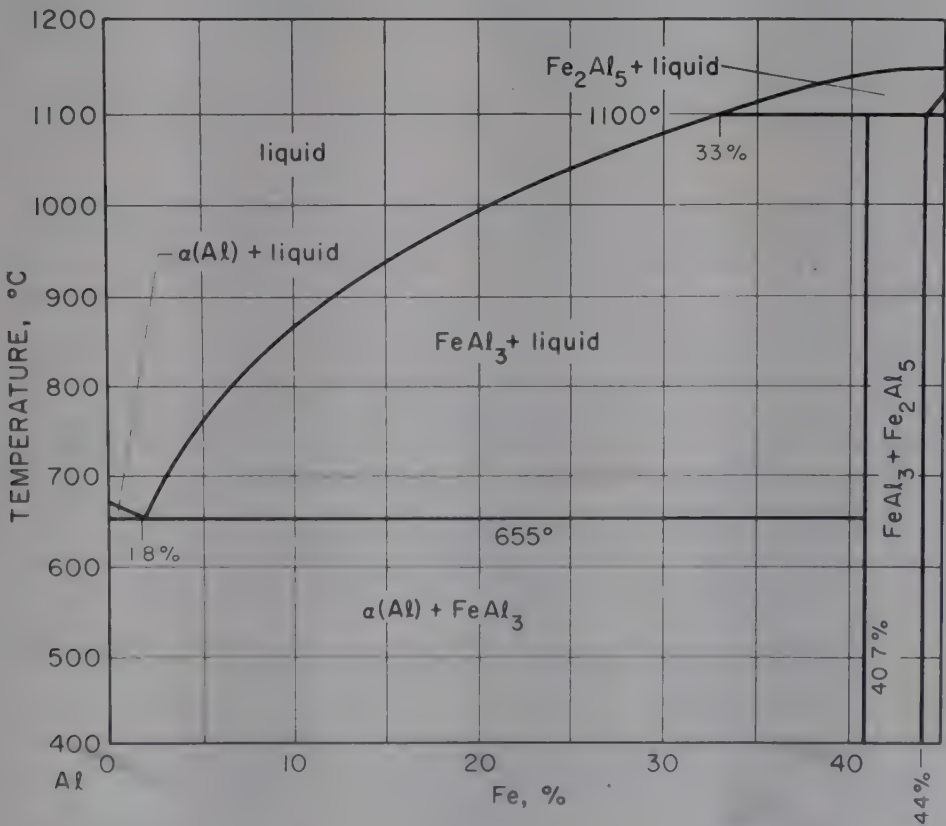
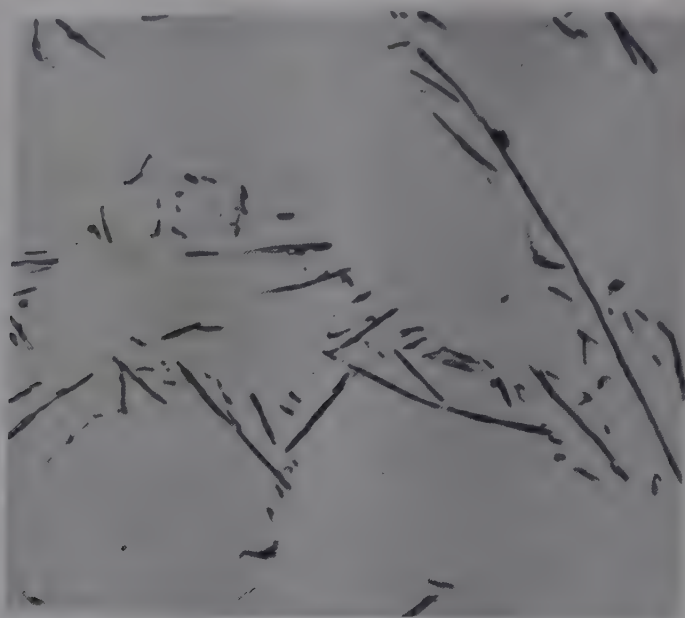


Fig. 8. Al-Fe phase diagram.

Fig. 9. Al₃Fe needles.

Al-Fe. Iron dissolves very easily in molten aluminum. When present in small amounts, it forms a eutectic with the aluminum at 1.8% of iron (Fig. 8). At the eutectic temperature the solubility in the solid state is very low, amounting to 0.03%, which decreases with decreasing temperature. The remainder of the iron forms, with the aluminum, a compound, FeAl₃, which appears in the form of needles and makes the metal brittle (Fig. 9). The Fe-Al alloys are of no practical interest.

Al-Si. The diagram shows a eutectic at 577°C whose solubility in the solid state is low (1.65%) at this temperature (Fig. 10). The solubility decreases to about 0.01% at room temperature. Thus, a more than negligible fraction of silicon tends to remain dissolved in the aluminum on rapid cooling of this metal after heating above 300°C. This silicon content appreciably increases the electrical resistivity of the

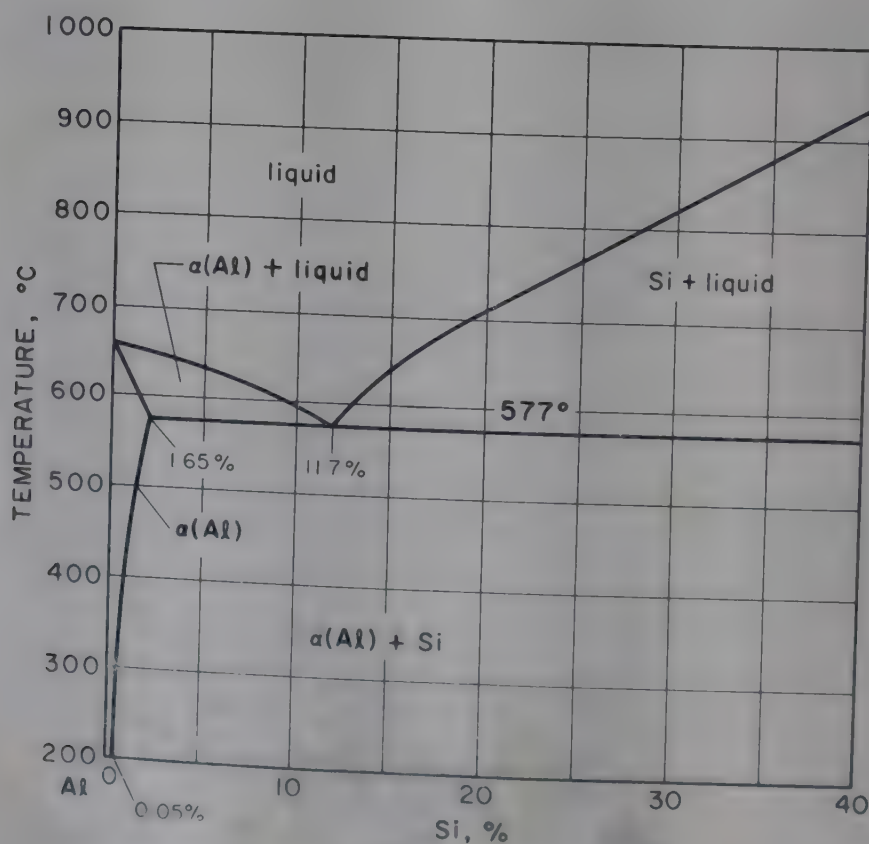


Fig. 10. Al-Si phase diagram.

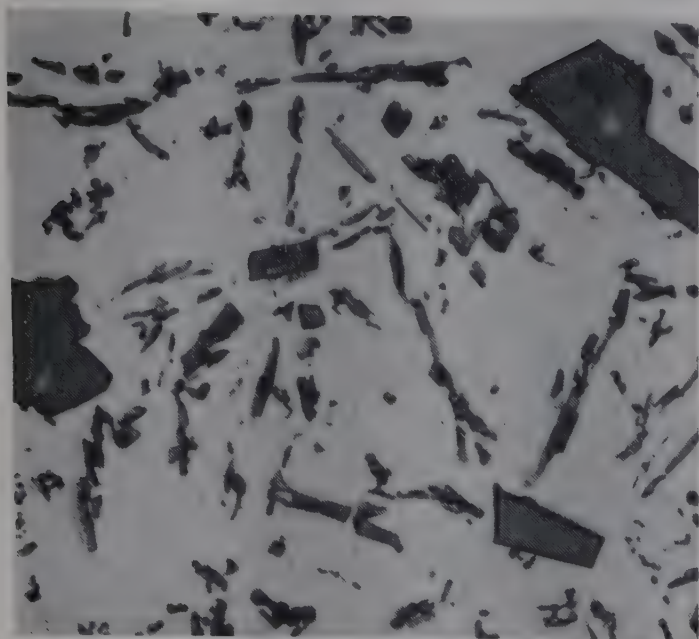


Fig. 11. Unrefined alloy containing 13% Si.

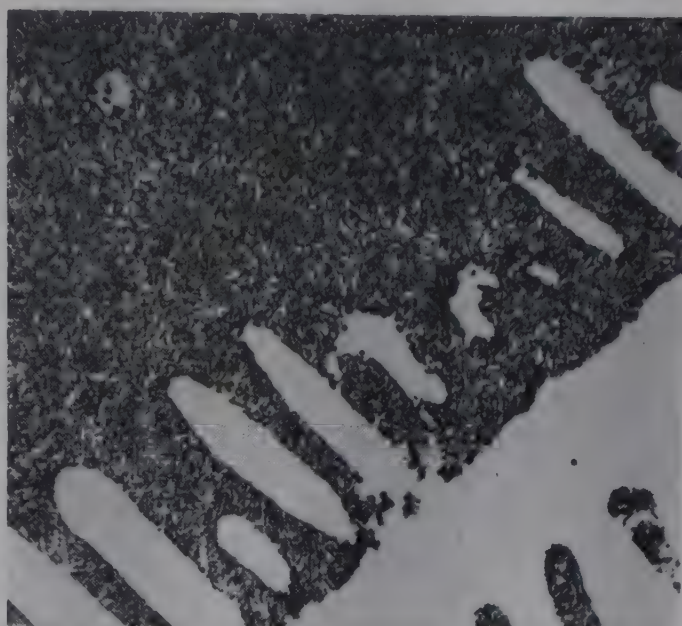


Fig. 12. Alloy containing 13% Si after refining with sodium.



Fig. 13. Unrefined alloy containing 20% Si.



Fig. 14. Alloy containing 20% Si after refining with phosphorus.

aluminum, a consideration that should be taken into account in the manufacture of wires for electrical conductors.

The eutectic alloy is of special interest from the practical point of view as it is easy to cast. When a small amount of sodium (0.05 to 0.08%) is added to the metal, the latter undergoes a structural modification of some interest: The silicon, instead of appearing in the form of rods and coarse particles, appears in the form of small rounded grains (Figs. 11, 12). In this condition, the metal shows elongation values from 9 to 12%, with ultimate strengths close to 18.5 kg/mm^2 (26,500 psi). The sodium is added either in the metallic state or by reaction with a flux which includes some sodium fluoride.

The linear coefficient of thermal expansion for Al-Si alloys decreases as the silicon content increases, and light Al-Si alloys are used for casting pistons or cylinder blocks. The primary silicon enclosed in hypereutectic alloys tends to take the form of needles, making such alloys brittle and difficult to machine. This form may be modified by addition to the metal of 0.01 to 0.03% phosphorus, either as copper phosphide or as red phosphorus (Figs. 13, 14).

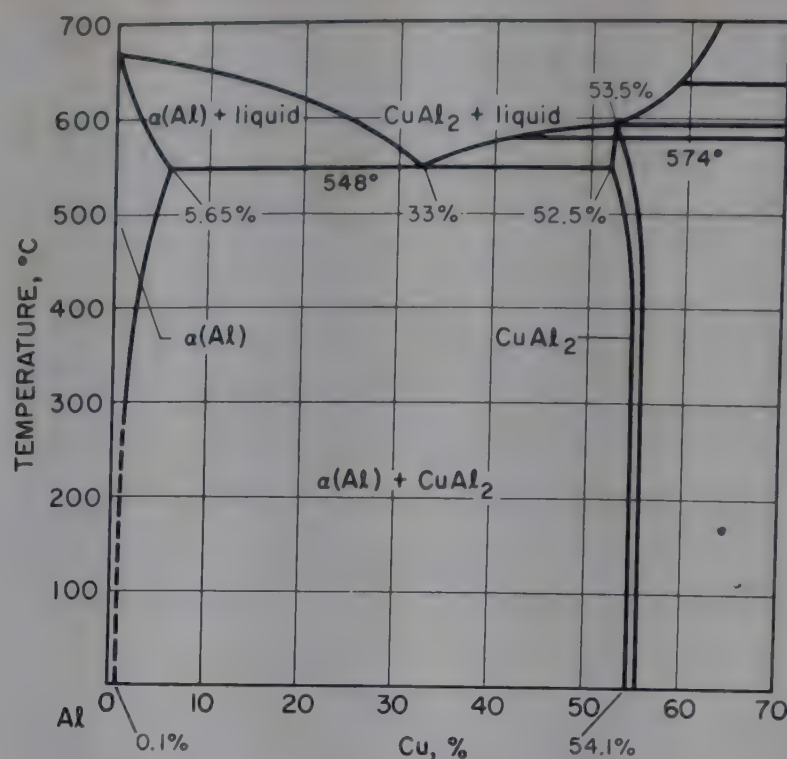


Fig. 15. Al-Cu phase diagram.

Al-Cu. The diagram for this alloy shows a eutectic on the aluminum side at 548°C (Fig. 15). At that temperature, a significant amount (5.65%) of the copper enters into solid solution in the aluminum. This solubility decreases rapidly down to room temperature (to 0.1%), but in alloys which include up to 4 or 5% of copper it is easy to keep the copper dissolved in the aluminum at room temperature. After heating of the alloy to approximately 500°C, rapid cooling will do the job. Reheating to a temperature between 100 and 200°C causes precipitation of the copper atoms. This appreciably improves the mechanical properties. This phenomenon is commonly used to obtain high-quality alloys, and copper happens to be one of the elements added most frequently.

Al-Mg. The Al corner of the Al-Mg diagram shows a eutectic that melts at 451°C. At this temperature 14.9% Mg remains dissolved in the aluminum, a quantity which decreases to, theoretically, 1.4% at room temperature (Fig. 16). Actually, even by slow cooling, up to 5% magnesium may remain in solid solution in aluminum. The alloys generally used are those which include 0.6 to 5% Mg, since their mechanical properties do not change appreciably, regardless of the rate of cooling after heating. These alloys are considered weldable even in thick pieces and, under certain conditions, completely corrosion-resistant in a marine environment (see under Corrosion, p. 977). As they also possess very good shaping qualities, and mechanical properties which are superior to those of pure aluminum, their use is extremely widespread.

Al-Zn. The solubility of zinc in aluminum is very great (Fig. 17), but as the resulting alloys are subject to intense intergranular corrosion in a damp atmosphere they find hardly any practical application. The ternary Al-Zn-Mg alloys are preferred to Al-Zn alloys because they have better mechanical properties and a far greater resistance to corrosion.

Al-Pb. It is interesting that lead in the liquid state is not miscible with aluminum if the lead content exceeds 1.8%, and that the solubility of solid lead in aluminum is very low. Moreover, solid lead forms spheres within the body of the solidified metal. This property is utilized to break the continuity of turnings when pieces are

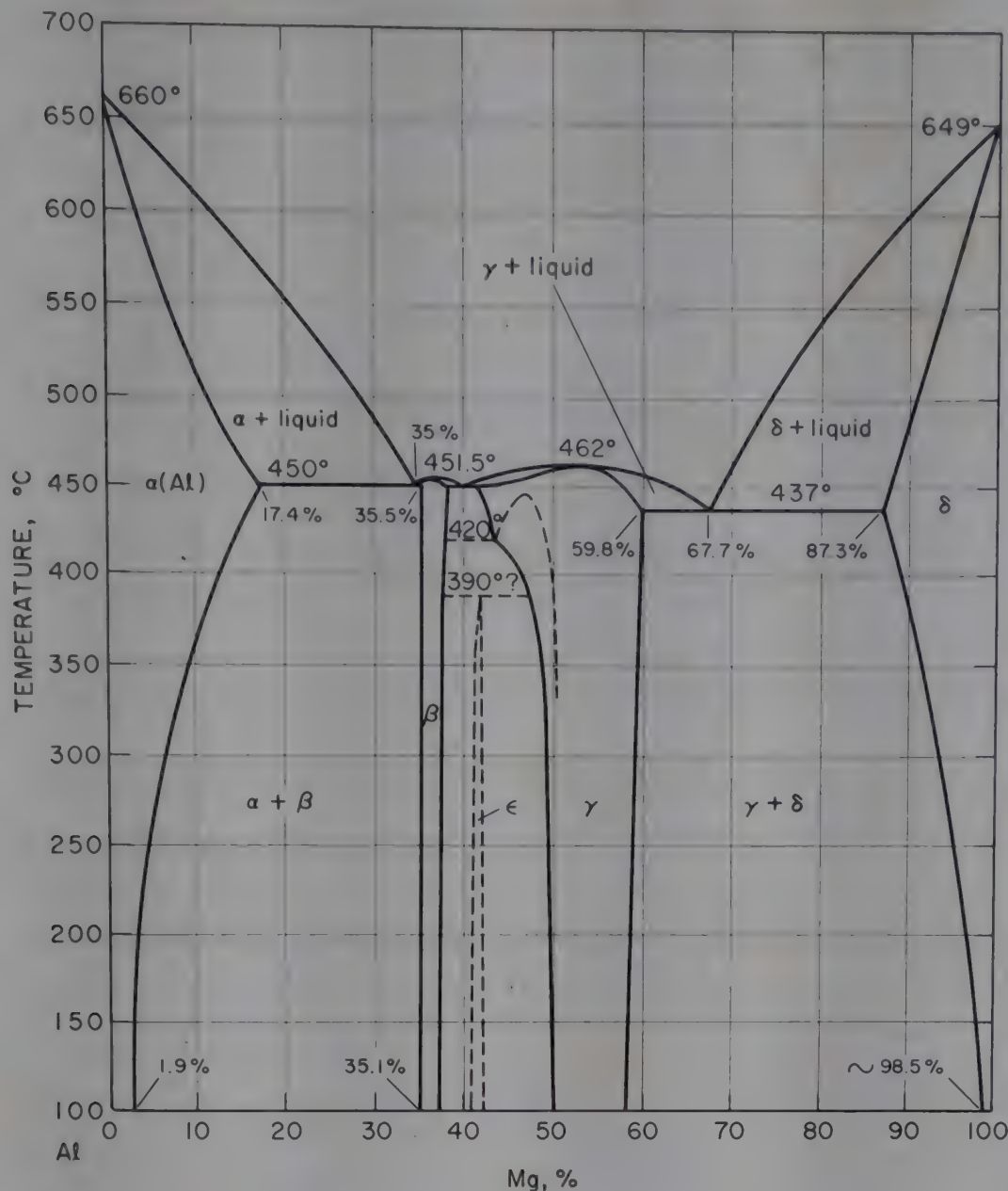


Fig. 16. Al-Mg phase diagram.

being turned on an automatic lathe. The type of alloy used (in France) is similar to the American 2014 and contains up to 1% lead.

Al-Bi. The same is true of bismuth as of lead. In the case of bismuth, the miscibility in the liquid state goes up to 3.36%.

Al-M_A (where M_A is an alkali or alkaline earth metal). Potassium and sodium are not soluble in aluminum at the melting temperature of aluminum. Some authors, however, have noted a very low solubility (0.002 to 0.003%) in solid aluminum at room temperature.

The presence of sodium in liquid aluminum reduces the solubility of hydrogen. But when sodium is present even in slight traces, it considerably impairs the rolling properties of certain alloys such as Al-Cu-Mg and, above all, Al-Mg. Magnesium fixes the sodium in the liquid metal and makes it difficult to eliminate.

Lithium forms the two binary compounds LiAl and Li₂Al. According to the most recent studies, lithium is slightly soluble in solid aluminum (0.005% at 100°C) and this solubility increases with temperature, up to 5.1% at 600°C.

Calcium forms two compounds with aluminum, an α -compound of still uncertain formula (Al₃Ca or Al₄Ca) and a β -compound, Al₂Ca. The presence of traces of calcium in commercial aluminum containing small quantities of silicon is advantageous

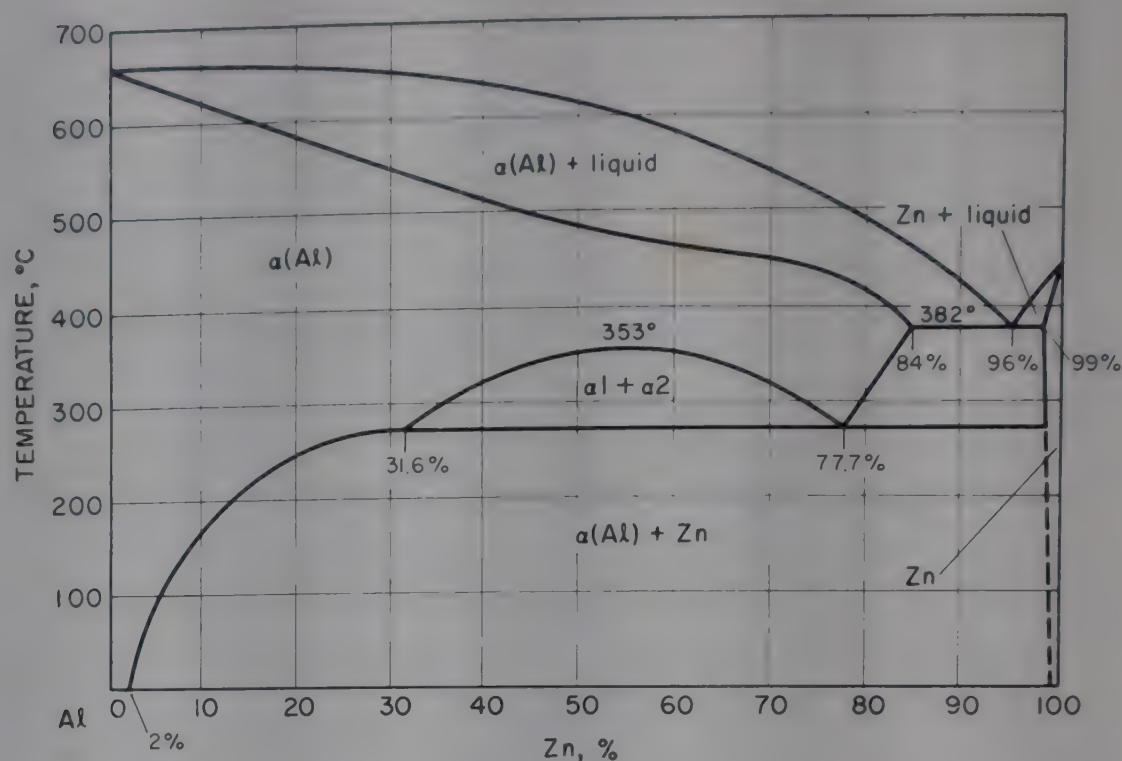


Fig. 17. Al-Zn phase diagram.

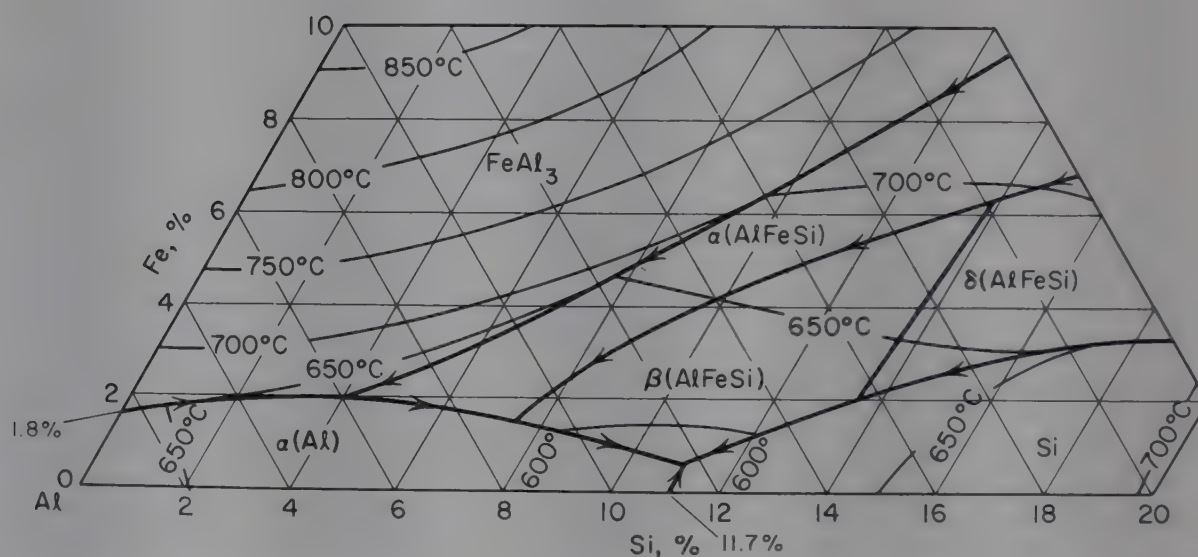


Fig. 18. Al-Fe-Si phase diagram showing the liquidus on the aluminum side.

in that the calcium increases the electrical conductivity of aluminum by combining with the silicon to form compound Ca_2Si . This prevents the possible solution of the silicon during the transformation of the metal. On the other hand, traces of calcium in excess of 0.010% should be avoided in foundry alloys containing 13% silicon, as they effect the shrinkage of the metal and increase the porosity of the pieces. Likewise their presence in certain rolling alloys (Al-Mg, Al-Cu-Mg) is harmful as it reduces their susceptibility.

Ternary Alloys. *Al-Fe-Si.* This diagram is due chiefly to the work of Gwyer and Phillips (20,21) as well as that of Fink and Van Horn (21a) and that of Jaeniche and Mondolfo (Fig. 18). It is of special importance since iron and silicon are always present in aluminum. Under the conditions here considered they form a binary phase Al_3Fe and three ternary phases of uncertain formulas, shown in Table 12 (22,23).

There is only one ternary eutectic point, which is very close to the binary eutectic Al-Si.

Table 12. Ternary Phases of Al-Fe-Si Alloys^a

Compound	Approximate formula	Fe, %	Si, %
α	$\text{Al}_{12}\text{Fe}_3\text{Si}$	32.12-32.45	8.41-10.32
β	$\text{Al}_9\text{Fe}_2\text{Si}_2$ or Al_5FeSi	26.65-27.18	13.82-14.93
δ	Al_4FeSi	25.4	25.5

^a See Figure 18.

The primary phases α , β , and δ can also be formed by peritectic reaction. The coordinates of the special points on the liquidus are given in Table 13 (24,25).

Table 13. Primary Phases of Al-Fe-Si Alloys^a

Point	Equilibrium reaction	Temperature, °C	Fe, %	Si, %
A	$\text{liquid} + \text{FeAl}_3 \rightleftharpoons (\text{Al}) + \alpha$	629	2	4
B	$\text{liquid} + \alpha \rightleftharpoons (\text{Al}) + \beta$	611	1.5	7.5
C	$\text{liquid} + \delta \rightleftharpoons \text{Si} + \beta$	595	2	13.6
D	$\text{liquid} + \alpha \rightleftharpoons \delta + \beta$	700	6.5	14
E	$\text{liquid} \rightleftharpoons (\text{Al}) + \beta + \text{Si}$	577	0.75	11.6

^a See Figure 18.

According to Armand the α region is in fact divided into three subregions which correspond to the three phases α_1 , α_2 , and α_3 , having the compositions,

Compound	Fe, %	Si, %
α_1	27.3	7.0
α_1	29.2	11.3
α_3	35.3	12.8

These phases introduce two other peritectic points, at 620 and 640°C, but since the results are still uncertain they have not been taken into account in constructing the diagram (Fig. 18).

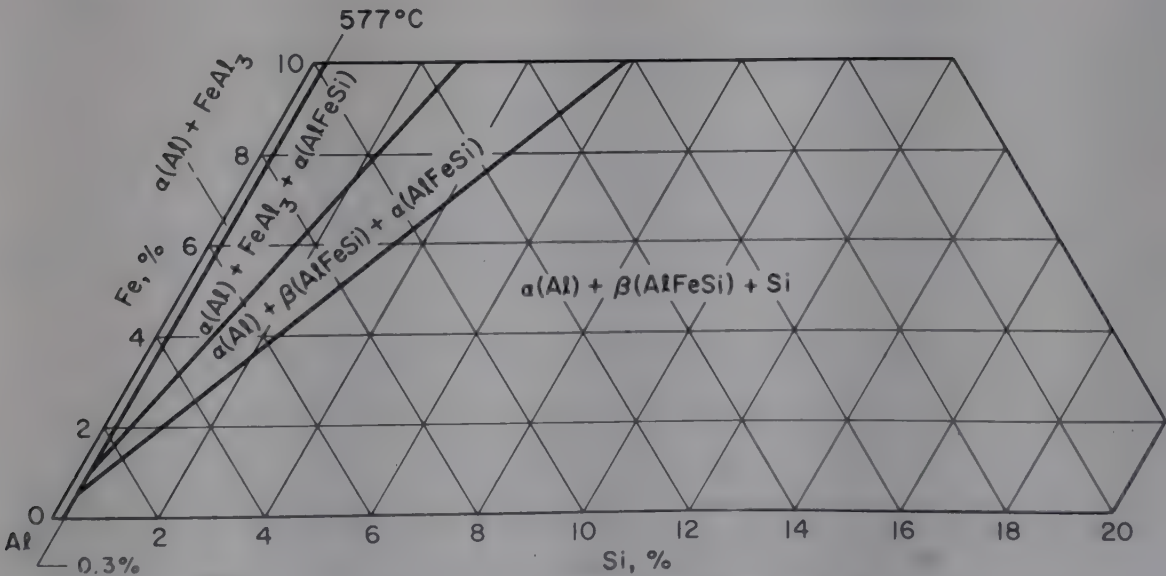


Fig. 19. Al-Fe-Si phase diagram showing the distribution of solid phases at equilibrium on the aluminum side.

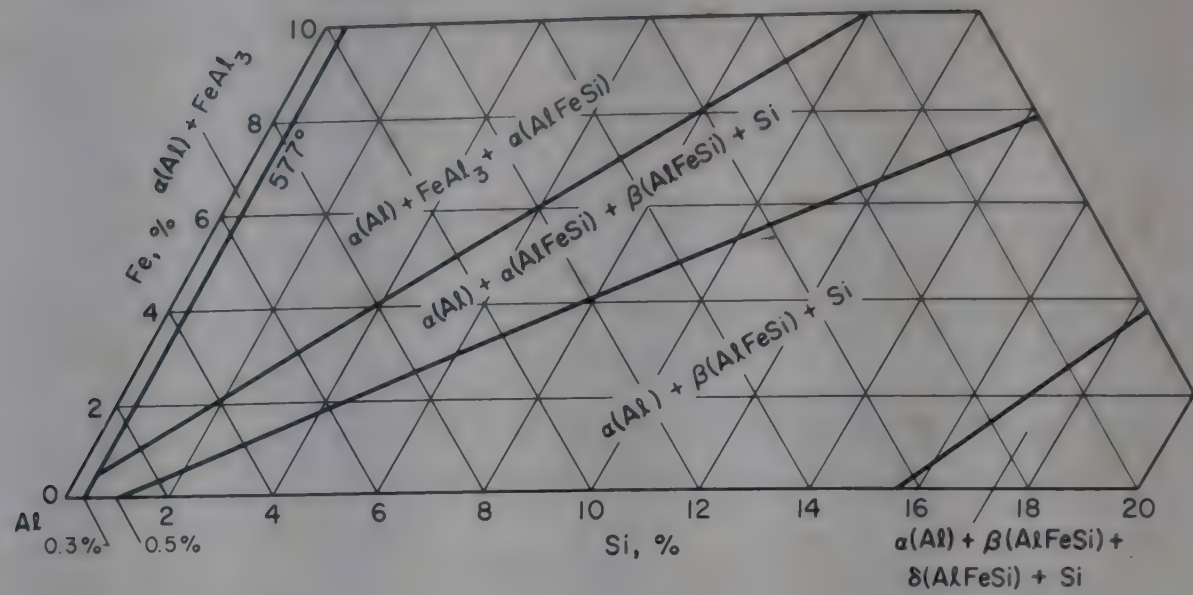


Fig. 20. Al-Fe-Si phase diagram showing the distribution of solid phases out of equilibrium on the aluminum side.

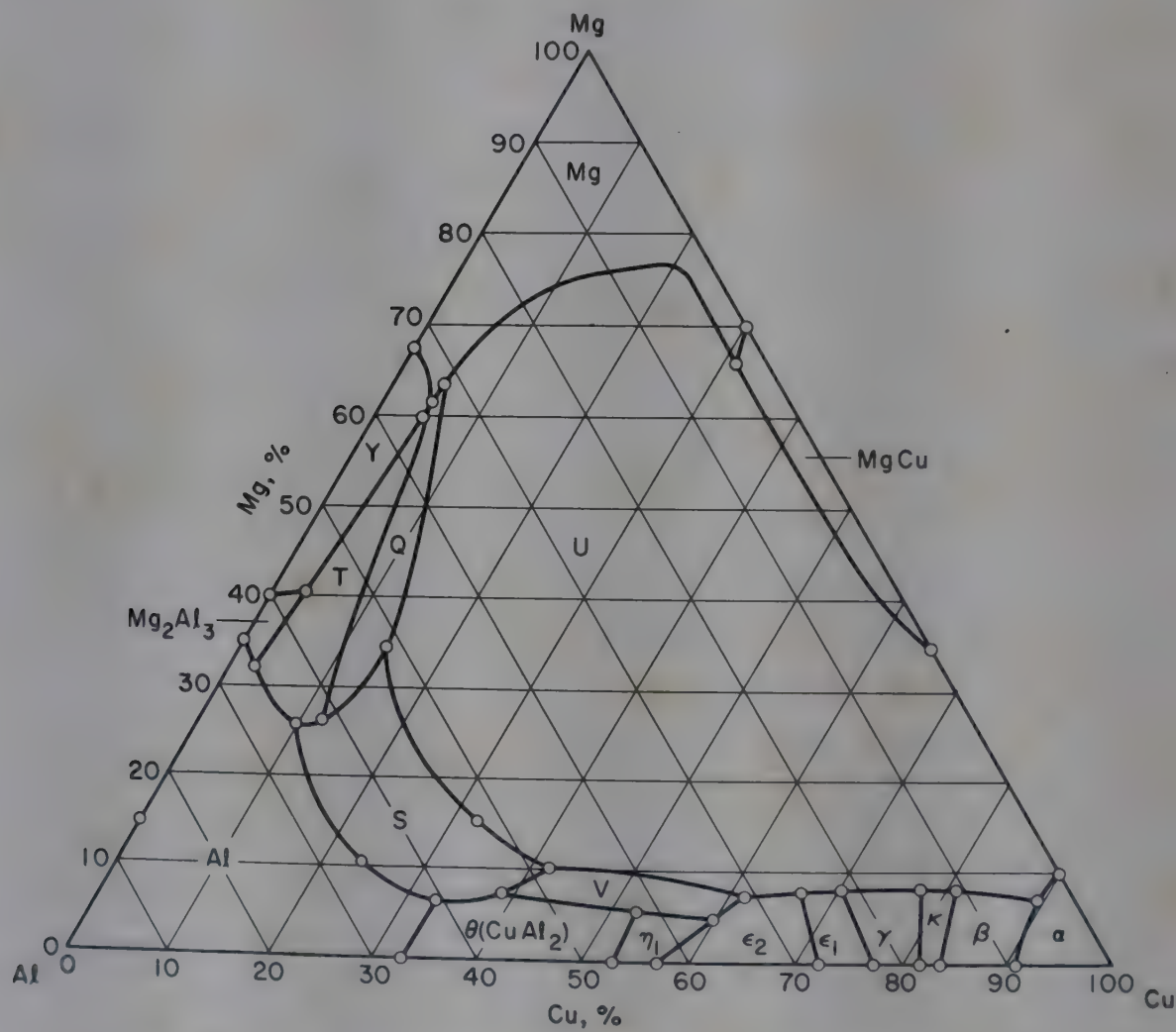


Fig. 21. Al-Cu-Mg phase diagram showing the liquidus.

Figure 18 is not much affected if small amounts of copper are present. On the other hand, the presence of manganese, cobalt, nickel, magnesium, or chromium, or copper within certain limits, deprives the diagram of any interest since the iron and the silicon then tend to alloy themselves with these elements instead of with one another. In the solid state and under conditions of equilibrium the phases present in the aluminum are distributed as shown in Figure 19. These conditions, however, are

seldom attained and generally the phases out of solution are more abundant, richer, in iron, and poorer in silicon (Fig. 20). If the metal is treated for 24 hours at 610°C to make it more homogeneous it is brought back closer to the equilibrium conditions.

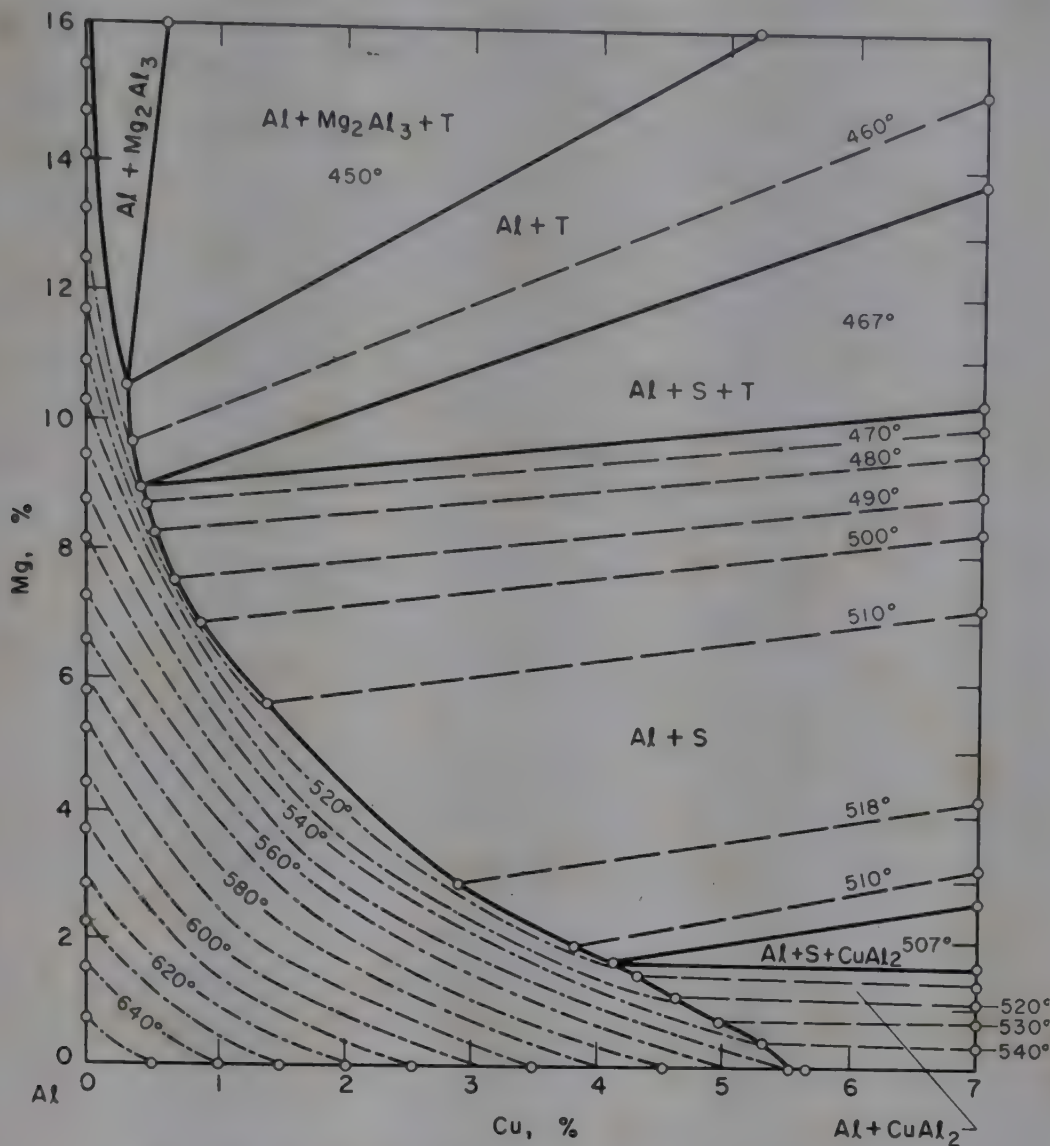


Fig. 22. Al-Cu-Mg phase diagram showing the solidus.

Al-Cu-Mg. This diagram (Fig. 21) is based on the works of Vogel (26) and Gayler (27). As amplified by the recent works of Mirgalovskaya and Urazov (28,29), it shows the existence of two binary phases,



and of five ternary phases, as follows:

T	Al_6CuMg_4	cubic
S	Al_2CuMg	base-centered orthorhombic
M or U	AlCuMg	hexagonal
Q or Y	$\text{Al}_7\text{Cu}_3\text{Mg}_6$	body-centered cubic
V	$\text{Al}_5\text{Cu}_5\text{Mg}_2$	cubic

In alloys which are rich in aluminum and which satisfy the conditions for equilibrium, the only constituents encountered above the solidus are CuAl_2 , S, T, and Al_3Mg_2 . If, however, solidification takes place rapidly the other phases may also be present.

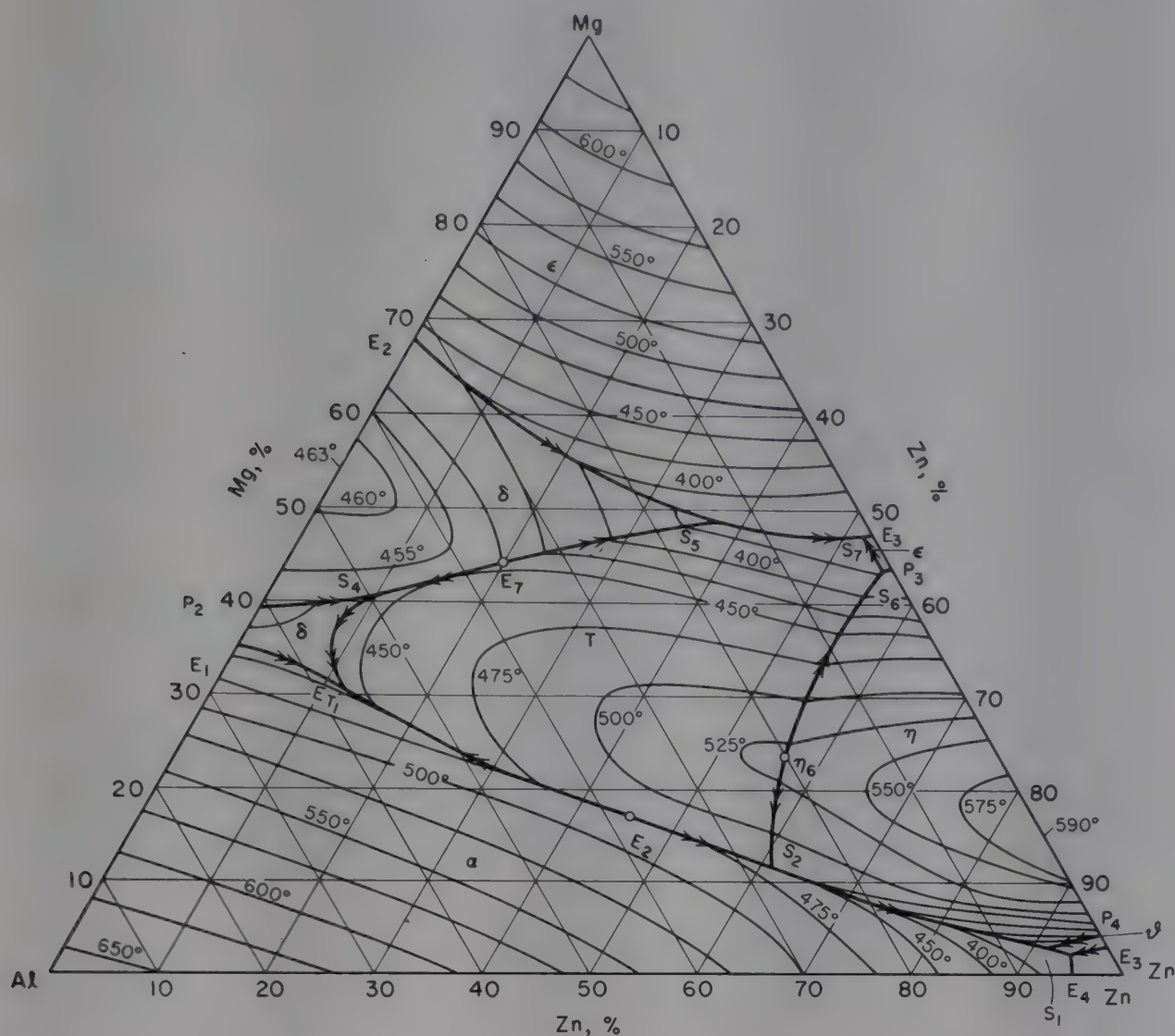


Fig. 25. Al-Mg-Zn phase diagram showing the liquidus.

Figure 22, which refers to alloys rich in aluminum, shows the shape of the solidus.

Figure 23 illustrates that there is a very great variation in the concentration of the aluminum-rich solid solution between the high temperature of the solidus and ordinary room temperature. Advantage has been taken of this to secure important modifications in the mechanical properties of such alloys by heat treatment. Generally, since silicon is present in the aluminum, the alloys in question are Al-Cu-Mg-Si rather than Al-Cu-Mg. Apart from the phases previously mentioned in the aluminum-based alloys, there appear the following binary and ternary phases,

binary phases: $\theta(\text{CuAl}_2)$, $\beta(\text{Al}_3\text{Mg}_2)$, Mg_2Si

ternary phases: $\delta(\text{Al}_2\text{CuMg})$, $\tau(\text{Al}_6\text{CuMg}_4)$

and one quaternary phase (30-33).

Figure 24 shows the section of the solidus for alloys containing 4% Cu at 510°C.

Al-Mg-Zn. This diagram (Fig. 25), in which the liquidus is based on the work of Köster, shows the existence of the binary phases Al-Mg and Mg-Zn as well as that of a ternary phase T to which the formula $\text{Al}_2\text{Mg}_3\text{Zn}_3$ (34,35) has been applied. As to binary phases, there is some risk of finding the β phase (Al_3Mg_2) and the η phase (MgZn_2) in alloys that are rich in aluminum.

Figures 26 and 27 give an idea of the shape of the solidus in the region shown and of the shapes of the limiting surfaces for solid solutions (36). The same remarks as were previously made apply to the possibility of improving these alloys by heat

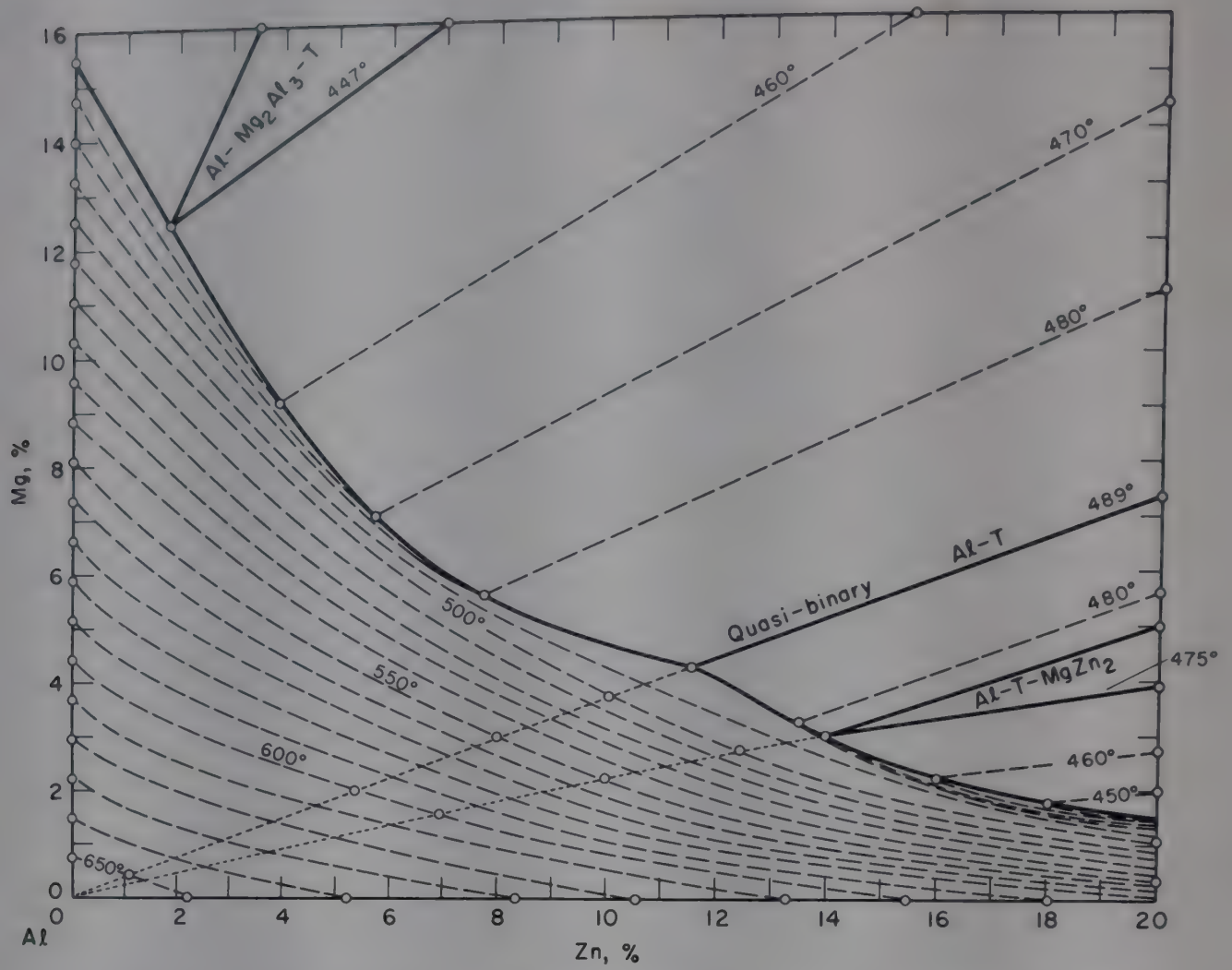


Fig. 26. Al-Mg-Zn phase diagram showing the solidus on the aluminum side.

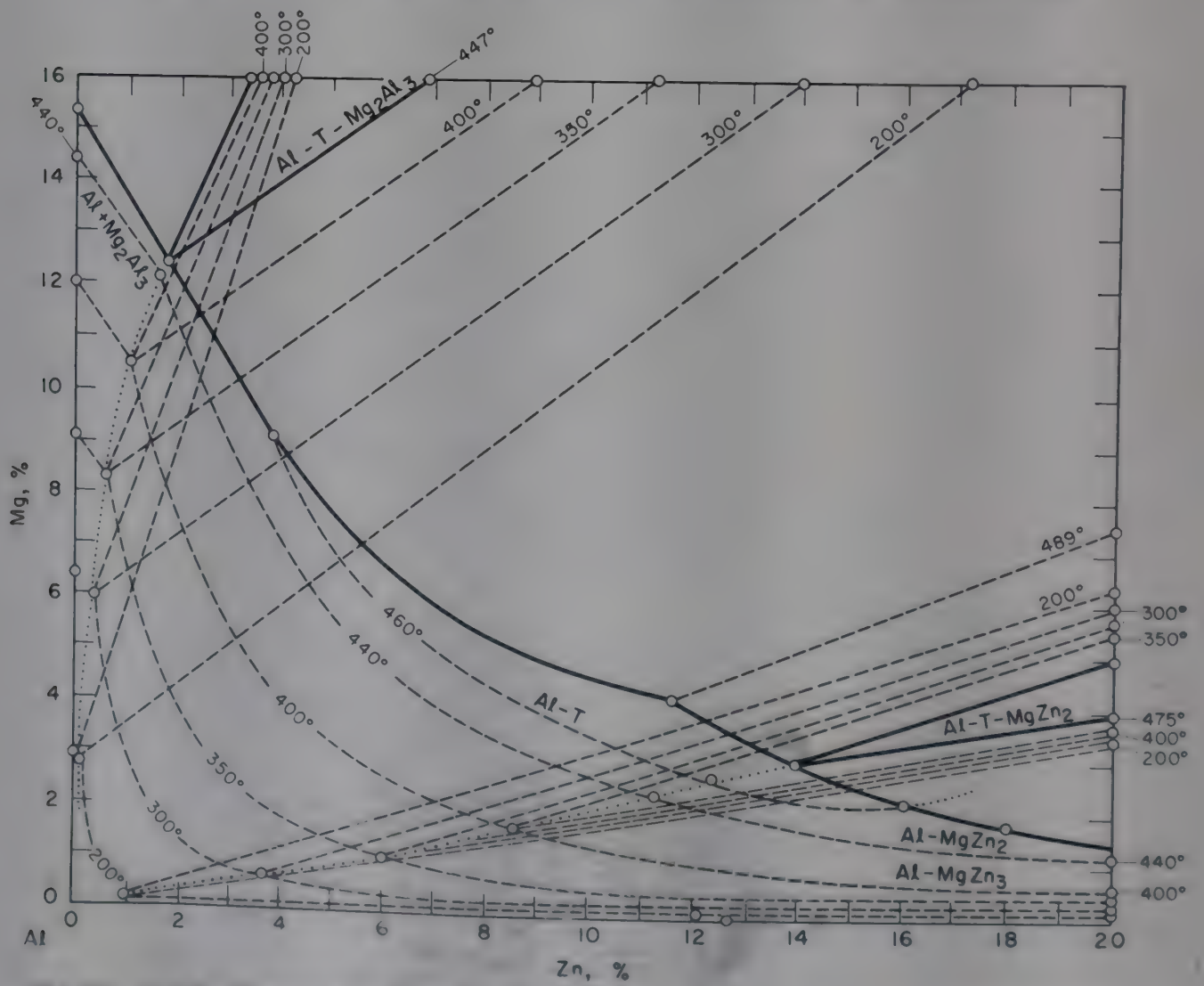


Fig. 27. Al-Mg-Zn phase diagram showing the limits of solid solutions on the aluminum side.

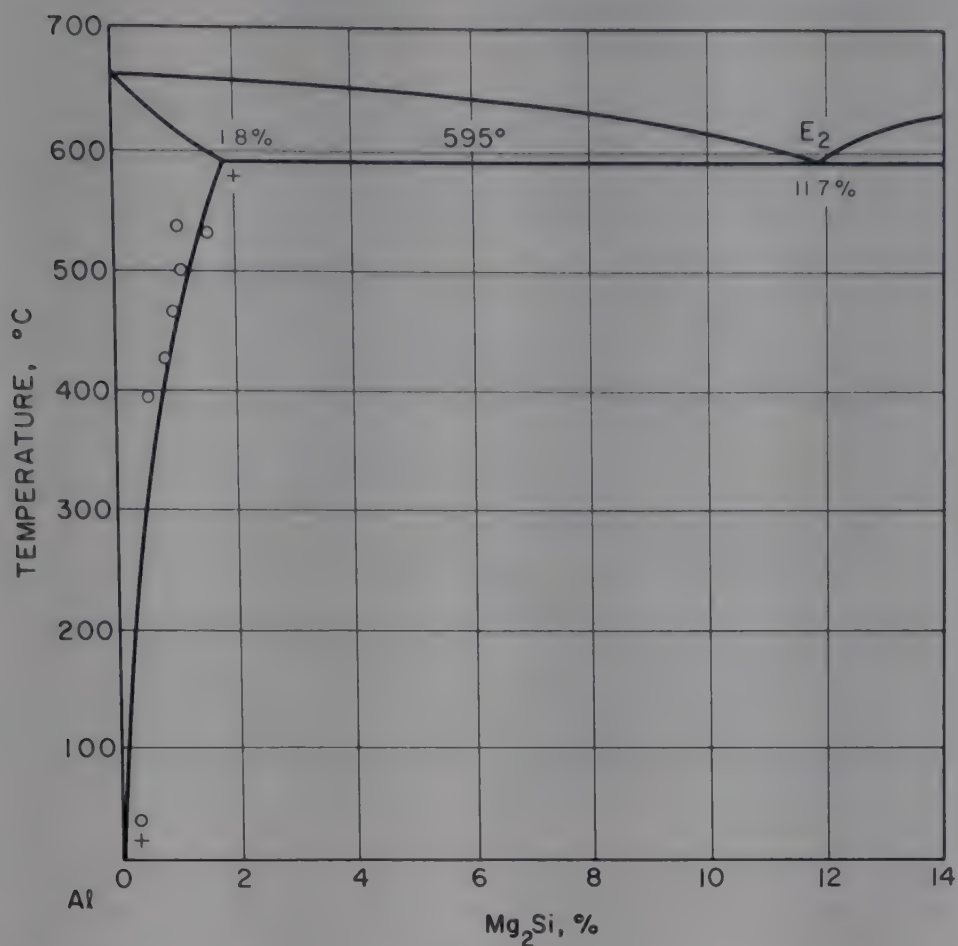


Fig. 28. Al-Mg-Si phase diagram for quasi-binary Al- Mg_2Si showing the limits of solid solutions.

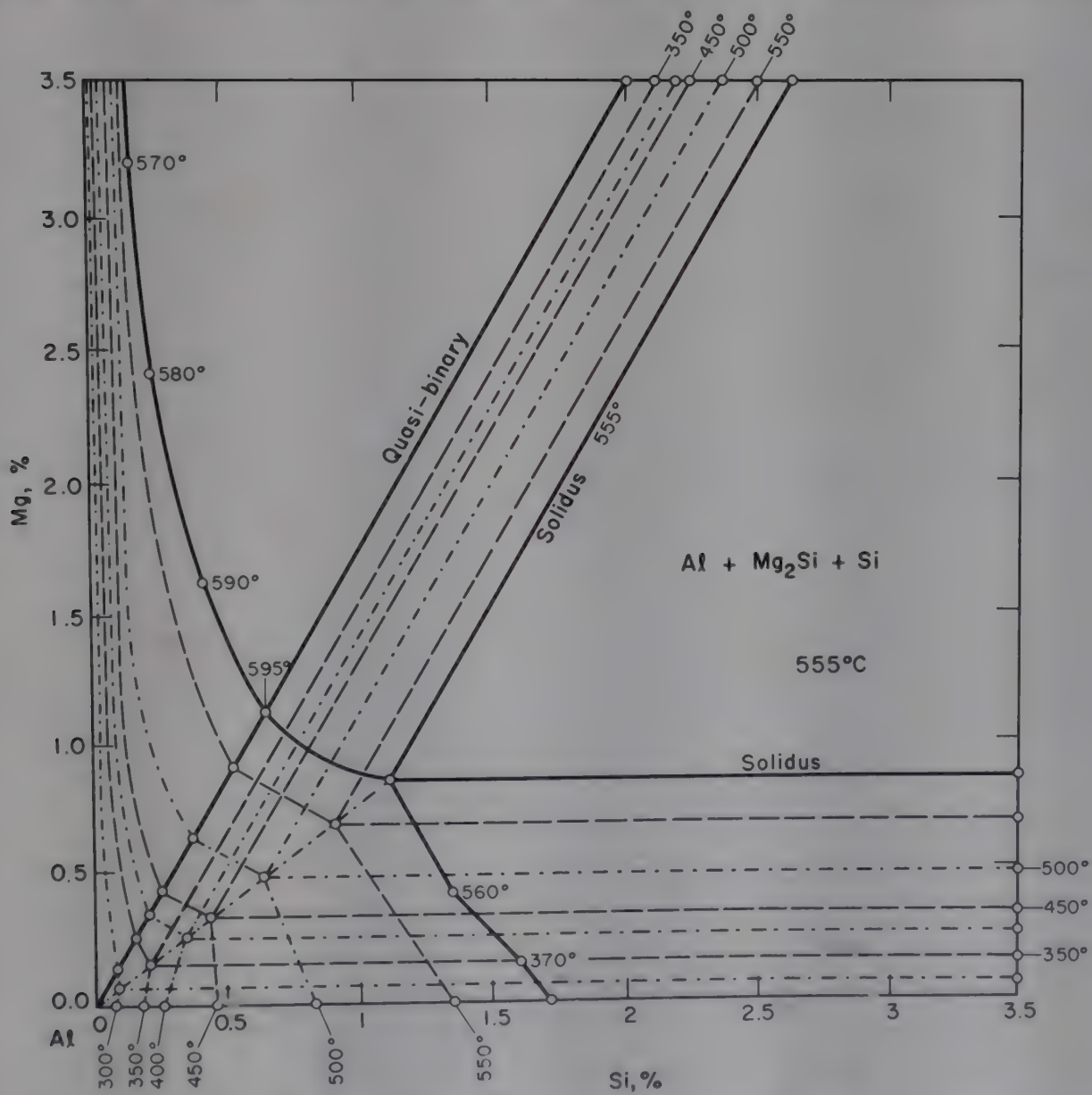


Fig. 29. Al-Mg-Si phase diagram showing the limits of solid solutions.

treatment. These alloys actually find wide application both for casting and as transformed alloys. It is among the heat-treated light alloys derived from the above by an addition of copper (0.5 to 2%) that the highest values for mechanical properties are found (37).

Al-Mg-Si. Magnesium and silicon form a compound which has an ionic character. Mg_2Si and the system $Al-Mg_2Si$, which is represented in Figure 28, may be considered as a binary diagram (38). It shows that the concentration of dissolved elements in the solid solution is governed strongly by the temperature. Once again, this has been used to advantage for modifying the alloys by heat treatment in order to improve their mechanical characteristics greatly.

An excess of silicon does not appreciably affect the solubility of Mg_2Si , whereas an excess of magnesium reduces it considerably; when the magnesium content reaches 3%, the solubility may be reduced to nil, whatever the temperature (Fig. 29) (17).

The phase diagrams of aluminum and other elements are less important and the interested reader may wish to refer to the specialized literature. *The Constitutional Diagrams of Alloys* by Haughton and Prince contains an excellent bibliography of the subject (39).

Heat Treatments

HOMOGENIZING

This treatment is applied to ingots and billets for forging and extrusion. It consists in prolonged holding (12 to 24 hours) at a temperature as close as possible to that of the solidus. This has the effect of reducing the segregations which occur at the boundaries of the grains, of making the concentration of the solid solution more uniform and, in certain cases ($Al-Mn$), of producing fine precipitation of the atoms dissolved in excess.

Homogenizing improves the hot-working properties of the metal, for instance, by permitting a greater speed of extrusion. It modifies the anisotropy of rolled products. Generally, it increases the plasticity, at room temperature, of metal which has been shaped either hot or cold, by increasing the elongation values and reducing the yield strength. It also improves the appearance of products after anodizing. For all these reasons, this treatment is frequently applied to cast aluminum ingots.

ANNEALING

Annealing is performed on products which have been subjected to cold working in order to reduce their yield strength and to increase their elongation. One may start from a cold-worked aluminum having the following mechanical properties:

yield strength	15 kg/mm ² (21,335 psi)
ultimate strength	17 kg/mm ² (24,180 psi)
elongation	5%

On heating, the metal then passes through the following states in succession:

1. Recovery, in the course of which the yield strength and the ultimate strength decrease very rapidly and the elongation values increase very considerably. The resulting mechanical properties are

yield strength	7.5–12.5 kg/mm ² (10,670–17,780 psi)
ultimate strength	9.7–14.5 kg/mm ² (13,800–20,625 psi)
elongation	35–12%

This means the disappearance of the cold-working stresses and an improvement in the internal structure of the subgrains.

2. Primary crystallization (or recrystallization), which is expressed in crystalline rearrangement and which leads to a state of maximum plasticity. Mechanical properties are

yield strength	4 kg/mm ² (5,690 psi)
ultimate strength	8 kg/mm ² (11,380 psi)
elongation	40–45%

3. Secondary recrystallization, or grain growth, which is produced only by intensive cold working and by high temperatures and which amounts to the excessive growth of certain grains at the expense of neighboring grains. This produces a reduction in elongation values.

The annealing is carried out in the temperature range corresponding to the second stage, that of recrystallization. So that this may not produce a grain too coarse to be acceptable, it must be applied to metal having a cold-working reduction of at least 20%. It is likewise desirable that the rate of temperature increase should be high, and it is preferred that sheets be annealed in continuous furnaces. The temperature reached by the metal must be carefully chosen; in the case of aluminum, it is usually between 310 and 350°C. For the alloys, it may be higher. For those alloys intended to undergo heat treatment and which are sometimes annealed for the purpose of destroying the effect of the previous treatment, cooling should be slow (50°C per hour) down to at least 200°C, in order to prevent these products from being affected permanently by the quenching.

SOLUTION TREATMENT, QUENCHING, NATURAL AGEING, AND ARTIFICIAL AGEING

This type of treatment takes advantage of the changes in temperature-solubility relationships that occur when certain alloying elements are added to the aluminum. As already mentioned, this affects particularly the alloys Al-Cu, Al-Cu-Mg, Al-Mg-Si, Al-Mg-Zn, and some more complex alloys derived from the foregoing (40).

Heating in the neighborhood of the solidus brings the maximum amount of these alloying elements into solution at that temperature. The effect of sudden cooling by quenching is that the dissolved atoms remain in solution even at room temperatures. This metastable equilibrium may disappear by itself if the metal is kept at room temperature for a long time (natural ageing), or if the metal is kept at a temperature of 100 to 200°C for several hours (artificial ageing).

For certain alloys (Al-Cu, Al-Cu-Mg, Al-Cu-Mg-Si) the quenching must necessarily be rapid, and in their case cooling is effected by immersion in water at a temperature which must not exceed 65°C. Otherwise, the quenching may be incomplete and, as a result, there might be a risk of the metal being subject to inter-crystalline corrosion. This also applies to certain Al-Mg-Zn-Cu alloys rich in zinc (7 to 8%). However, a lower cooling rate may be adequate for some other alloys (Al-Mg-Si; Al-Mg Zn-Cu with 5% Zn) and, for those, cooling in moving air may be

sufficient. For yet others (such as Al-Mg-Zn) natural cooling of the pieces may suffice, an advantage when it is desired to make welded pieces.

Quenching softens the alloy and ageing (natural or artificial) improves the mechanical properties. In the use of aluminum alloys, advantage is taken of this temporary softening of the metal for giving manufactured pieces their shape. Hardening does not occur until later.

Natural ageing is slower the lower the temperature maintained: Below 0°C it takes place only very slowly, but at 20°C it is completed from within four days to three months, depending on the alloy. Al-Mg-Zn alloys require the longest time of natural ageing.

As a rule artificial ageing gives the metal a higher yield strength and a higher ultimate strength, but a lower ductility, than does natural ageing. Fatigue strength is about the same in both cases. Corrosion resistance is generally not as good after artificial ageing.

If Al-Cu-Mg alloys which have been quenched and aged naturally are heated for a short time (5 to 10 minutes) at 200°C , the effect is first to soften the metal and, in some cases, this is used for shaping. The alloy then regains its normal hardness, but does so very slowly. This phenomenon, known as reversion, has not yet been satisfactorily explained. On the other hand, the mechanism involved in the hardening of certain aluminum alloys by ageing after quenching has been clarified during recent years.

This hardening was first ascribed to the fine precipitation of the intermetallic compound which had disappeared when the metal was heated prior to quenching. Actually, it takes place immediately before this stage. The studies of Guinier in France (41) and of Preston in England (42), based on the technique of x-ray diffraction by monocrystals, have shown that the dissolved atoms began to collect in aggregates at very low ageing temperatures (below 100°C). These aggregates, called Guinier-Preston zones or, in the English literature, GP1 zones, differ from each other according to the nature of the dissolved atoms.

The GP1 zones of Al-Cu alloys are flat, their thickness amounts to a few angstroms, and their diameter attains up to a hundred angstroms. In the case of Al-Mg₂Si alloys, the zones are threadlike and are aligned along the [100] axis of the matrix (43). In both these cases the GP1 zones are oriented with respect to the lattice of the matrix. In the case of Al-Mg-Zn alloys (44), they are spheroidal and have a diameter of approximately 50 Å. It is generally assumed that the hardening of the alloy takes place at the moment at which these zones appear. The most recent theories, however, postulate that structural defects, such as vacancies, occur before this stage is reached.

The intermetallic compound itself appears only at relatively high ageing temperatures (175 to 200°C) and is always accompanied by a diminution of hardness. The development between these two stages (GP1 zones and intermetallic compound) is rather complex and differs in the case of different alloys, as follows:

1. In the case of Al-Cu alloys the flat aggregates become thicker and may then be discerned under an electron microscope. These aggregates are called GP2 zones, in the English literature, or the θ'' phase, in the French literature (45). Following the θ'' phase, an intermediate tetragonal θ' phase appears, in the form of epitaxial plates on the faces of the cube in the matrix. Only after this does precipitation occur in the θ phase (CuAl_2).

2. In the case of the Al-Mg₂Si alloys, at 150°C, the aggregates are threadlike and arrange themselves with the same periodicity as the matrix. Then, at 200°C, they flatten and it is only at 300°C that the Mg₂Si precipitates.

3. In the case of Al-Mg-Zn alloys, the MgZn₂ phase appears at 100°C in the form of planes, ordered in relation to the matrix. At 200°C, a disordered precipitation of MgZn₂ occurs.

STABILIZING TREATMENTS

These are treatments which have the effect of stabilizing an alloy either (1) in regard to its mechanical characteristics or (2) dimensionally or (3) as regards its susceptibility to intercrystalline corrosion.

In the first case, such treatments are applied to, for instance, cold-worked Al-Mg alloys. Heating for 4 hours at 190°C, without producing recovery, imparts mechanical properties to the metal which it will retain permanently.

In the second case, these treatments are carried out on cast pieces made from alloys intended to be used at temperatures where ageing would normally occur in consequence of the incomplete solution which always obtains after the metal has solidified. Pistons and engine castings are typical examples of such pieces. This ageing is accompanied by variations in relative length of the order of 1×10^{-6} which may lead to seizure of the moving parts. Heating for a few hours at 200°C prevents this trouble.

In the third case, which is peculiar to Al-Mg alloys containing 4% Mg or more, the object of the treatment is to prevent accidental heating close to 100°C from bringing about an abnormal tendency to intercrystalline corrosion. This danger can be avoided by prolonged heating at 250°C.

Fabrication of Aluminum Alloys

Aluminum and its alloys are frequently employed in the manufacture of finished articles, worked by all known methods. Processes of fabrication include casting in sand or in permanent molds or under pressure, rolling, extrusion, wiredrawing, forging, stamping, pressing, deep drawing, spinning, all types of welding, riveting, and adhesive bonding.

MELTING AND CASTING

As aluminum melts at 660°C, this metal and its alloys are easy to melt in flame-heated furnaces fed by gas or oil, but they may also be melted by electrical resistance or induction heating. An excellent practice adopted in some large aluminum foundries consists in melting the metal in flame furnaces and then maintaining it for several hours in an electric furnace. This helps to free the metal from gas.

Molten aluminum becomes covered with a thin continuous film of oxide which prevents any further oxidation. If alkali or alkaline-earth metals are present, the thickness of this film is increased, but if beryllium is present, even in trace amounts (0.003%), the thickness of the film is reduced.

The use of a flux may be extremely useful in some cases, as, for instance, to obtain fine grain or to remove some undesirable impurity. As an example of the first of these objectives, mention may be made of the grain control obtained in aluminum rolling ingots by the use of a flux which contains potassium fluotitanate. Sometimes potas-

sium fluoborate is added to this flux. The titanium boride formed as a result is very effective for grain refining.

An example of the second objective is the reduction in the titanium content of aluminum by treatment with potassium fluoborate. This compound, used in amounts equal to ten times the weight of titanium contained in the aluminum to be treated causes titanium boride to form. The titanium boride collects at the bottom of the furnace.

It may also be mentioned that aluminum fluoride reacts with any calcium and magnesium contained in the aluminum, and is sometimes used to eliminate those elements when their presence is undesirable. An example is the elimination of calcium from an alloy containing 13% Si. Aluminum fluoride is used mixed with potassium chloride and sodium chloride.

Finally, there are covering fluxes which prevent the metal from dissolving any gas during exposure to an atmosphere likely to contain moisture. A good formula for such a composition is as follows: NaF or AlF₃.3NaF, 10 parts; KCl, 45 parts; NaCl, 45 parts.

The furnace linings are chosen so that they will not react on contact with molten aluminum. From this point of view magnesia, although expensive, is the ideal lining; there also are satisfactory linings of silicoaluminous brick very low in silica.

Liquid aluminum rapidly dissolves iron if not protected by a suitable refractory layer. It attacks cast iron less rapidly than iron. Cast iron (from hematite) or containing silicon is the most resistant but it is wise to protect this also.

Rolling ingots and billets are generally obtained by the semicontinuous casting

Table 14. Aluminum Casting Alloys: Chemical Composition and Type of Casting^{a,b,c}

U.S. alloy	Similar alloys in other countries				Composition (U.S.A.)				
	France (AFNOR)	U.K. (BS)	Germany (DIN)	Italy (UNI)	Fe	Si	Cu	Mg	Others
43 ^{a,b}		LM-18				5.0			
85 ^a	A-S5U3	LM-4				5.0	4.0		
319 ^{a,b}		LM-21		3052		6.0	3.5		
356 ^{a,b}	A-S7G		G-AlSi ₁₀ Mg	3599		7.0		0.3	
360 ^c	A-S10G	LM-9	G-AlSi ₁₀ Mg	3051		9.5		0.5	
A 132 ^b	A-S12UN	LM-13				12.0	0.8	1.2	2.5 Ni
380 ^c						8.5	3.5		
47 ^{a,b}	A-S13	LM-6	G-AlSi ₁₂	3047		12.5			
108 ^a			G-AlCuSi			3.0	4.0		
142 ^{a,b}	A-U5NT	LM-14		3045			4.0	1.5	2.0 Ni
122 ^{a,b}	A-U10G	LM-12		3041	1.2		10.0	0.2	
138 ^b	A-U10S4			3042		4.0	10.0	0.3	
A 214 ^b	A-G4Z							3.8	1.8 Zn
214 ^a	A-G3T	LM-5	G-AlMg ₂	3059				3.8	
218 ^{a,c}	A-G6		G-AlMg ₂	3058				8.0	
220 ^a	A-G10	LM-10		3056				10.0	

^a Sand casting. ^b Permanent molding. ^c Die pressure casting.
NOTE: Similar alloys (in countries other than the U.S.A.) are molded in the same way as their U.S. counterparts.
LEGEND: AFNOR, Association Française de Normalisation; BS, British Standards (for engineering purposes); DIN, Deutscher Industriennormen; UNI, Unificazione Nazionale Italiana.

process. This process consists in solidifying the metal within a ring of aluminum sheet which is cooled externally by spraying or by a water jacket, and evacuating the metal progressively at the lower part of the ring, as solidification takes place in the upper part.

A variation of this process consists in making the metal solidify in the form of a continuous strip. In the Hazelett process the liquid metal is inserted between two cooled metal bands which carry it with them in a rotary movement. In the Hunter Engineering process, as in that of P  chiney, the metal is cast between cooled cylinders of a rolling mill, vertically in one case, and horizontally in the other. In the Properzi and Rigamonti processes the liquid metal solidifies between a steel ribbon and a wheel, the rim of which is shaped to the section desired.

In the design of molds for the casting of light alloys, the low specific weights of these metals must be allowed for, as this factor does not help in removing gases from the mold or in filling the voids left by shrinkage. It must also be remembered that the shrinkage is considerable (the linear casting contraction for unalloyed aluminum being 1.7% and, for its alloys, 1.1 to 1.4%).

Table 15. Aluminum Casting Alloys: Mechanical Properties and Type of Casting^{a,b,c}

Alloy	Condition	Yield strength ^d	Ultimate strength ^d	Elongation, %
43 ^a	≠	8	19	8-3
43 ^b	≠	9	23	10-2.5
85 ^c	≠	24	40	3
319 ^a	≠	18	27	2
	T6	24	36	1.5-2
319 ^b	F	19	27	2
356 ^a	T51	20	25	2
	T6	24	33	3-3.5
356 ^b	T6	27	40	3-5
360 ^c	F	23	41	5
A 132 ^b	T551	28	36	0.5
	T65	43	47	0.5
380 ^c	F	26	43	2.0
47 ^a	F	11	26	7
108 ^a	F	14	21	1.5-2.5
142 ^a	T21	18	27	1
	T61	40	41	
142 ^b	T571	34	40	1
	T61	42	47	0.5
122 ^c	T2	20	27	1
122 ^a	T61	40	41	0.5
122 ^b	T551	35	37	
	T65	36	48	0.5
138 ^b	F	24	30	1.5
A 214 ^b	F	16	27	2.5-7
214 ^a	F	12	25	9
218 ^c	F	27	45	8
220 ^a	F4	25	46	14

^a Sand casting.

^b Permanent mold casting.

^c Die pressure casting.

^d In 1000 psi.

LEGEND: T, temper; F, as cast.

The problem of inserting wrought iron or cast iron pieces into aluminum castings has been solved by the Al-Fin process, which consists in covering the iron piece with an aluminum layer 0.02 to 0.03 mm thick before immersing it in an aluminum bath, with or without an addition of silicon or zinc. Other processes which do not necessitate a metallic bond have been proposed, such as cladding of the rough pieces by pressure casting (iron casting by centrifugation is an example).

The aluminum plating of iron wires or sheets may be effected by a continuous treatment. Primarily two methods are in use for preparing the surface of the iron immediately before its immersion in the liquid aluminum. One of these consists in oxidizing the iron by heating at 900°C and in then reducing the oxide film by hydrogen (Sendzimir process). The other employs a flux of potassium fluozirconate to apply a new coating to the work after pickling. Sometimes a small quantity of silicon (2%) is used to reduce the thickness of the layer of intermetallic diffusion, as well as small quantities of beryllium (0.2%) which likewise reduces oxidation of the liquid metal.

For the chemical composition, type of casting, and mechanical properties of aluminum casting alloys see Tables 14 and 15.

PLASTIC DEFORMATION

Hot working is usually carried out at temperatures between 350 and 500°C. If the metal is too cold it is not pliable enough and if it is too hot it is made brittle by the melting of a small quantity of the eutectic between the dendrites.

Hot rolling is performed in rolling mills driven by powerful motors. The rolls are cooled by ample spraying with an emulsion; this also causes a fatty film to form, preventing the hot metal from adhering to the surface of the rolls. One or several reversing mills are employed and, in modern plants, the second step in hot rolling is performed on a three- to six-stage tandem mill.

After the metal has been annealed it is cold-rolled, preferably in a four-high mill which may or may not be in tandem and which has been lubricated abundantly. The lubricant must be chosen with some care, since it not only must have good lubricating properties but must not cause corrosion or spots during the annealing process.

Thin aluminum sheets are rolled in four-high mills which have polished cylinders and which are run at surface speeds of up to 3000 meters per minute. The last passes are performed in double thickness, and final thicknesses of 5 to 7 microns may thus be obtained. This is thinner than wrapping paper, which is usually 10 microns thick.

Extrusion finds wide application as a process of manufacture because it permits the use of inexpensive tools to obtain very varied and sometimes very complicated shapes. The property of being weldable by pressure, characteristic of those alloys that contain only a small amount of added elements (Mg, in particular), makes it possible to produce sections with internal cavities of complicated shapes. The hydraulic presses used for this work are capable of exerting up to 15,000 tons of pressure.

Forging may be started either from ingots or billets cast by the continuous process or from metal preformed by extrusion. Powerful equipment is necessary as the forging alloys, at their working temperature, have an elastic limit higher than that of iron at its own forging temperature. Hence, light alloys are forged in presses with compressive forces of up to 50,000 tons. Removal of the metal from the matrices has to be facilitated by designing them appropriately.

Table 16. Wrought Aluminum Alloys: Chemical Composition^a

Similar alloys in other countries							U.S. composition of wrought alloys, %								
Alloy type	U.S.A. (AA)	Canada (CSA)	France (AFNOR)	Ger- many (DIN)	Italy (UNI)	U.K. (BS, DTD)	Fe	Si	Cu	Mn	Mg	Cr	Ni	Zn	Ti
Al	1100	HA.X.990	A4	Al 99	P-APO	1C	...	1.0	...	0.20	0.05			0.10	
Al-Mn	3003	.M1	A-M1	3.0515	3568	N3	0.7	0.6	0.20	1.0-1.5				0.10	
Al-Mg	5005		A-G0.6	3.3515	3573		0.7	0.40	0.20	0.20	0.5-1.1	0.10		0.25	
	5052		A-G2	3.3525		N4	...	0.45	...	0.10	2.2-2.8	0.15		0.10	
	5056	GM-50R	A-G5	3.3555	3576	N6	0.40	0.30	0.10	0.05-0.20	4.5-5.6	0.05-0.20		0.10	
														0.25	0.15
Al-Mg-Si	6061	GS-11R	A-SG	3.2315		H30	0.7	0.40-0.8	0.15-0.40	0.15	0.8-1.2	0.15-0.35		0.10	
	6063	GS.10	A-GS	3.3206	3569	H9	0.35	0.20-0.6	0.10	0.10	0.45-0.9	0.10		0.25	0.15
Al-Cu-Mg	2014		A-U4GS	3.1325	3581	H15	1.0	0.50-1.2	3.9-5.0	0.40-1.2	0.20-0.8	0.10		0.25	
	2024	CG.42	A-U4G1	3.1355	3583	H14	0.50	0.50	3.8-4.9	0.30-0.9	1.2-1.8	0.10		0.10	0.02-0.10
	2219		A-U6MG				0.30	0.20	5.8-6.8	0.20-0.40	0.02		0.9-1.2	0.10	0.04-0.10
	2618		A-U2GN			H18	0.9-1.3	0.25	1.9-2.7		1.3-1.8				
Al-Mg-Zn	7075	ZG-62	A-Z5GU	3.4365	3737	DTD-687A	0.7	0.50	1.2-2.0	0.30	2.1-2.9	0.18-0.40		5.1-6.1	0.20
	7178		A-Z8G5		3738	DTD-5074	0.7	0.50	1.6-2.4	0.30	2.4-3.1	0.18-0.40		6.3-7.3	0.20

^a For each alloy, in addition to the elements shown, there may be 0.05% each of miscellaneous others, up to a total of 0.15%.

LEGEND: AA, The Aluminum Association; CSA, The Canadian Standards Association; AFNOR, Association Française de Normalisation; DIN, Deutsche Industrienormen; UNI, Unificazione Nazionale Italiana; BS, British Standards (for engineering purposes); DTD, British Standards (established by the Ministry of Aviation).

Aluminum also lends itself to impact extrusion, a process which makes it possible to manufacture hollow pieces with thin walls (such as collapsible tubes and cans for food products). This process has been greatly developed in recent years. The compressive force of the presses in use reaches up to 800 tons and their working speed ranges from 40 to 120 strokes per minute.

Sheets may be shaped by various procedures that include either hot or cold pressing, stamping over metal or rubber forms, or bending.

Wrought Alloys. Tables 16 and 17 show the composition and mechanical properties of the principal aluminum alloys used for shaping.

Table 17. Wrought Aluminum Alloys: Mechanical Properties

U. S. alloy and temper	Tensile properties					Shear strength ^a
	Yield strength ^a	Ultimate strength ^a	Elongation, %		Hardness, Bhn ^b	
			On sheets	On rods		
1100-O	5	13	35	45	23	9
1100-H18	22	24	5	15	44	13
3003-O	6	16	30	40	28	11
3003-H18	27	19	4	10	55	16
5005-O	6	18	30		28	11
5052-O	13	28	25	30	47	18
5052-H38	37	42	7	8	77	24
5056-O	22	42		35	65	26
5056-H38	50	60		15	100	32
6061-T5	21	35	22	25	65	24
6061-T6	40	45	12	17	95	30
6063-T6	31	35	12		73	22
2014-T4 bare	42	62		18	73	38
2014-T6 bare	60	70		13	86	42
2014-T4 clad	37	61	22			37
2014-T4 clad	60	68	10			41
2024-T4 bare	47	68	19	20	120	41
2024-T6 clad	42	64	19			40
2219-T6	44	61		13	120	
2618-T6	47	63		13	125	
7075-T6 bare	73	83	11	11	150	48
7075-T6 clad	67	76	11			46
7178-T6 bare	88	78	10	11	155	52
7178-T6 clad	81	71	10			49

^a In 1000 psi. ^b Brinell hardness number.

METHODS OF JOINING

Welding. Aluminum and its alloys are readily joined by several welding processes including those based on the use of oxyacetylene, oxyhydrogen, a metal arc, an inert-gas-tungsten arc, and a gas-metal arc. The oxide film on the aluminum is readily removed by wire brushing prior to welding by any of the arc processes. A flux (generally a fluoride, such as LiF-NaF) is employed only with the oxyacetylene process, which is seldom used today.

Although virtually any aluminum alloy can be welded, those most commonly welded include Al-Mg, Al-Mg-Mn, Al-Mg-Zn, and Al-Mg-Si alloys.

Brazing. This technique takes advantage of the low melting points of alloys containing 9 to 13% Si (575°C). The flux generally used in torch brazing contains zinc chloride (ZnCl₂), which lowers the melting point and enables the flux to react with the metal to be brazed, forming a surface film of zinc which facilitates the operation. Brazing can be carried out by immersion in a molten salt bath and this may aid in the production of complicated pieces, such as radiators, heat exchangers, and the like. Special aluminum sheets coated with films of Al-Si alloy have been developed to facilitate this method of joining.

Soldering. In soldering aluminum use is made of Al-Zn alloys which may contain Cd, Sn, and other metals. This mode of joining is apt to be susceptible to intercrystalline corrosion by moisture in the air.

Electric Welding. Aluminum alloys can be either spot-welded or welded with a roller electrode. The high thermal conductivity of the metal necessitates very short welding times; as a result, a very heavy current and special machines are needed.

Pressure Welding. Aluminum may be welded to itself by pressure alone, provided this causes enough deformation to bring about relative displacement of the surfaces to be joined. By this process, aluminum may also be welded to copper without producing a brittle joint.

Riveting. This method is very much used in aircraft construction to join pieces that cannot be welded. In some countries the alloys used for this purpose contain no more than 3% copper and, by virtue of their having a longer natural ageing time than, say, the U.S. alloy 2024 (see Tables 16, 17) make the work easier.

Adhesion. Adhesives have become widely used, following their extensive development by the chemical industry. As the curing of resins suitable for adhesives generally involves heating up to 175–200°C, this heat may also be utilized to bring about artificial ageing of the joined pieces.

Corrosion

Many applications of aluminum take advantage of its stability in aqueous media or in air, even sea air. Aluminum owes this stability not to its place in the electro-motive series but to the surface coating of alumina which protects it.

Table 18 shows the potentials for solution according to Von Zerleeder, measured against a standard calomel electrode in an aqueous solution of 2% sodium chloride (45a).

According to this table aluminum should not be considered a very noble metal. This means it is fairly susceptible to galvanic corrosion, so that contact between it and

Table 18. Solution Potentials (Von Zerleeder)

Metal	Potential, mv	Metal	Potential, mv
magnesium	−1600	lead	−480 to −500
zinc	−1050	tin	−450 to −470
5%-Mg alloy	−770	copper	−200
3%-Mg alloy	−760	silver	− 50 to + 50
Al-Mg-Si	−760 to −800	mercury	0
Al-Mn	−740	stainless steel	+100
Al-Si	−700 to −730	gold	+200
iron	−650	platinum	+240
Al-Cu-Mg	−580 to −605		

other susceptible metals (with which it might constitute a couple in which it would act as the anode) should be avoided.

Contact with copper, lead, nickel, iron, silver, or graphite is usually disastrous. Contact with stainless steel may also prove quite harmful, but this depends essentially on the conditions of exposure. Contacts with zinc or cadmium may or may not be safe, depending on the pH of the solution.

It may, thus, be seen that connections between unlike materials which include aluminum or its alloys call for special consideration so as to avoid direct contacts. Among ways of doing so, coating of the nonferrous metal with a metal less noble than itself (such as cadmium or zinc) may be mentioned. Another device is to interpose an insulating material that will not take up moisture, as by brushing with pitch or asphalt or with primary coatings based on zinc chromate.

Similar couples (as the ones described above) may arise in alloys which always have a more or less heterogeneous structure. This is the reason why aluminum-copper alloys are among those most subject to corrosion. Al-Zn-Mg alloys, especially those with a large zinc content, may be subject to atmospheric corrosion. A double precaution is therefore needed, firstly, ageing at a temperature in excess of 135°C and, secondly, protection. Alloys containing 1 to 5% Mg, on the other hand, comprise a range of alloys which resist corrosion provided the thermal conditions of their manufacture have not been such as to favor intercrystalline corrosion. This latter generally occurs in pieces having a high magnesium content (4 to 6%) and which, after rapid cooling, have accidentally been brought up to temperatures of 75 to 150°C. When the pieces are likely to be affected in this way it is advisable that the annealing be followed by very slow cooling or by a special thermal treatment (see under Heat treatments, p. 968).

Where the conditions of use will be very severe, recourse is had to cathodic protection by cladding the sheets of Al-Cu-Mg or Al-Mg-Zn alloys with a thin layer (5 to 10% of the thickness) of an aluminum alloy more anodic than themselves. For instance, sheets of Al-Cu-Mg may be coated with Al and sheets of Al-Mg-Zn with a layer of Al-Zn alloy to the extent of 1 or 2% of their own thickness; these coating materials should be as free as possible from copper. This protection is effective even if the protective layer is destroyed over an area as much as an inch in diameter.

Aluminum itself may be strongly attacked by industrial waste waters, especially if they carry traces of copper or lead from pipes or valves made of those metals and preceding it in the hydraulic circuit. Pipes protected on the face in contact with the water by a layer of Al-Zn alloy containing 1 to 2% Zn may be used to advantage.

As deionized water may attack commercial aluminum, its pH should be kept within definite limits (5 to 6).

Finally, stray electric currents which may cause contact corrosion should be avoided.

Surface Treatments

Surface treatments may be used to clean a surface, to protect it against corrosion, or for decorative effect.

DEGREASING AND PICKLING

The traditional form of pickling, which is very effective but often considered too harsh, is to use a 5-10% caustic soda solution in a range between room temperature

and 70°C. This must be followed by neutralization with dilute nitric acid. A much less active treatment, which, however, dissolves the surface layer of the alumina perfectly, is that of using a solution containing 15% by weight of sulfuric acid and 5% by weight of chromic acid.

Before painting, often no more is done than solvent degreasing or alkaline degreasing, followed by light pickling in an acid bath. For better performance, it is sometimes necessary to precede the painting by treatment with a complex salt containing both aluminum chromates and phosphates.

ENGRAVING

Decorative engraving is done by using a solution which usually includes ammonium bifluoride or nitrates. This gives the metal a fine silky texture.

CHEMICAL OXIDATION

The processes employed are meant chiefly to give the right surface conditions for subsequent varnishing or painting, rather than to provide the metal directly with a protection against corrosion. Basic baths (MBV (or Modified Bauer-Vogel) baths, which are alkaline chromate solutions) are used in some processes; acid baths (Alodine baths, also known as Alocrom baths in Great Britain and in the U.S.A., which contain phosphoric acid in a chromate solution), in others. In point of fact it is less a question of providing an oxide layer than a layer of complex salts, such as the double phosphate of chromium and aluminum.

ANODIZING

Aluminum connected to the positive pole of a source of current, and immersed in an electrolyte along with a cathode of lead or graphite, is coated with alumina according to the reaction



This coating is formed by a boundary layer of a thickness approximately 8 to 13 Å per volt, which is not porous but is covered over by a porous layer of anhydrous alumina (the diameter of the pores being 100 to 400 Å). The thickness of this coating depends not only on the amount of electricity (coulombs) used in the operation, but also on the nature of the electrolyte and, therefore, its ability to redissolve the deposit already formed, as well as on the temperature. Furthermore, by controlling the conditions of electrolysis, it is possible to obtain coatings of predetermined thickness and hardness.

If the oxidized work is left in water at 100°C for a few minutes, the anhydrous alumina formed is transformed into boehmite (hydrated alumina); the pores are thereby sealed and the coating loses its porosity.

The electrolyte most generally used for this electrolysis is a 15–20% aqueous solution of sulfuric acid (having a specific gravity of 98% H_2SO_4). The density of the current is approximately 1 to 2 amp/dm². Under these conditions, at 20°C, a layer 12 to 15 microns thick is deposited in 30 minutes. This layer is colorless but can be dyed, before being sealed, by organic or inorganic coloring baths. It affords excellent protection against corrosion in media with a pH between 4.5 and 8.5. The porosity of this deposit before sealing is used to advantage not only for coloring but to make the

deposit absorb lubricants, varnishes, or photosensitive films that permit photographic images to be registered on the metal.

The thickness of the coatings used varies according to the purpose to be served. A layer one-half micron thick makes an excellent base for bonding to paints. The coatings used in architecture for the outsides of buildings have thicknesses of 15 to 22 microns. Thick layers of no less than 50 to 100 microns are formed in a bath whose temperature does not exceed 0°C and these offer excellent resistance to abrasion.

Flexible deposits, serving for the electrical insulation of aluminum wires and strips, are obtained by adding to the bath 1 to 3% of sodium chloride and using an alternating current at current densities of 100 to 200 amp/dm².

Aluminum alloys can be colored directly by anodic oxidation; the alloy which contains 4 to 5% of Si becomes gray and that which contains 0.5% of Cr acquires a golden hue. These colors are completely resistant to light, and products treated in this way are employed in architecture. The same result may be obtained by replacing the sulfuric acid used with sulfosalicylic acid (the Kalcolor process); according to the alloy, this produces colors ranging from golden (in Mg alloys) to black (in Mn alloys).

Sealing, which destroys this porosity, must be carried out in pure water free from certain anions, such as phosphate. Tap water can be used. Nickel or cobalt acetate is added. Adding potassium bichromate to the sealing water appreciably increases the protection which these oxide layers afford against corrosion, especially on Al-Cu-Mg alloys.

POLISHING AND BRIGHTENING

Electrolytic polishing and brightening comprises another anodic operation. This serves to dissolve the projecting roughnesses, whereas the concave parts are protected against the action of the electrolyte by a viscous layer. There are many kinds of processes for doing this, such as the Brytal process (with sodium carbonate and phosphate), the Jacquet process (perchloric acid with acetic anhydride), the Alzak process (fluoroboric acid), and the Pollectro process (phosphoric acid with a sulfuric acid-chromic oxide mixture).

Chemical polishing and brightening is carried out in baths which include both an oxidant and a reagent capable of dissolving the alumina formed. Generally, the oxidant is nitric acid, and the reagent for dissolving the alumina may be phosphoric acid (in the Alupol and Othalu baths) (46) or, for instance, (as in the Erfwerk bath), ammonium difluoride.

Chemical or electrochemical polishing only serves to give the surface a high reflecting power; neither of them protects it. Surfaces so treated should, therefore, be subjected to a light anodic oxidation in a sulfuric acid bath; this provides a transparent deposit so as to preserve the excellent optical properties of the surface.

ELECTROPLATING

Depositing another metal directly on aluminum presents difficulties because of the alumina film, which has to be removed in order to achieve proper adhesion between the two metals. A general answer to this problem, which is applicable to many alloys, is to provide an intermediate coating with zinc. This zinc coating is obtained by chemical means, the zinc being transferred from a solution of sodium zincate. This solution also includes potassium cyanide for refining the grain of the zinc deposit.

It is also recommended, after a first layer has been formed, to dissolve it in nitric acid and to deposit a second layer that will be considerably finer and more adhesive than the first. The second layer may be coated further with subsequent layers of, for instance, nickel followed by chromium and then silver.

METALLIC COATINGS

The processes described below refer to metallic coatings applied by chemical means.

Nickel Coating. The Kanigen process, which depends on the decomposition of nickel hypophosphite, is applicable to aluminum. Better results are obtained when it is preceded by a double coating with zinc, such as described above. To obtain a very high corrosion resistance, the deposit should be at least 50 microns thick. The deposit is also very hard.

Tin Coating. Tin may be deposited directly by decomposition starting either from an acid bath in the presence of fluorides or from a solution of sodium stannate. This coating greatly improves the frictional properties of aluminum. It has been used to coat moving parts, such as bearings and pistons.

VARNISHING AND PAINTING

Food containers of aluminum are varnished to protect the metal. This operation is carried out continuously on the strip from which the cans are afterwards cut out and stamped. This makes it necessary for the varnish to be very adhesive and able to withstand autoclaving. The preparation of the metal strip consists simply in degreasing it in a solution of sodium phosphate and carbonate, but more uniform results are obtained by following up this operation with light anodic oxidation, which makes the oxide film on the metal perfectly homogeneous. The varnishes used are of the epoxy-phenol or modified epoxy-vinyl type, if it is desired to have a deposit capable of going through the autoclave, or of the vinyl type if all that is wanted is a layer which will withstand pasteurization (as for fruits, or fruit juices, for instance).

Paints may be applied either on finished pieces or by a continuous process on strips of aluminum or its alloys. After careful degreasing of the metal, the latter has to be passivated. Certain chemical treatments (of the types Alodine 400, Alodine 1200 or 1200 S) give excellent passivation and make the coats of paint very adherent so that they can withstand deformation by bending, stamping, embossing, or other means.

Protection against corrosion by humidity may be improved by coating with a primer between the metal so prepared and the paint itself. The best primers are those based on zinc chromate and synthetic resins.

If no esthetic quality but merely very good corrosion protection is sought, it may be sufficient to brush the products with a bituminous varnish, which affords perfect insulation from the ground or from cement or plaster.

PORCELAIN ENAMELING

Enamels which melt at a low temperature have recently been introduced especially for use on aluminum and its alloys. They are fired at the annealing temperature of the metal. If the alloy in question is one that can be hardened by air quenching and subsequent ageing, it is enough to make it cool quickly in order to accomplish

hardening. This method of coating is currently employed on Al-Mg-Si alloys. Its use is being developed in architecture and in making domestic utensils.

Uses

The uses of aluminum are based on its physical properties: light weight combined with excellent thermal and electrical conductivity, the high mechanical strength of certain alloys, the versatility of its optical properties, the ease with which it can be shaped and machined, its freedom from toxicity, and its excellent corrosion resistance.

DOMESTIC UTENSILS

One of the earliest uses for aluminum was to make saucepans. There have been some complaints that aluminum blackens on contact with hot water, but this discoloration disappears when the contact is prolonged. The blackening is due to the formation of a very thin film of alumina, whose dichroic properties disappear as it thickens. In any case, this discoloration is absolutely free from danger, as is proved by the universal use of such utensils without any harmful effects. Recently, aluminum kitchen utensils internally coated with Teflon have appeared on the market. Teflon prevents sticking (see Abherents); the coating also reduces the thermal conductivity at the surface of the metal and thus permits the more uniform heating of foodstuffs.

Aluminum is widely used for making juice squeezers and many other kitchen utensils. It also finds application in the construction of washing machines, vacuum cleaners, refrigerators, and many other appliances.

CHEMICAL AND FOOD INDUSTRIES

Aluminum not only offers the great advantage of freedom from attack by many chemical products, but also of having colorless salts which do not constitute a risk of impairing the appearance of the products with which the aluminum comes in contact. The good thermal conductivity of aluminum leads to its use for constructing many forms of heat exchangers.

Aluminum is employed in the construction of equipment for manufacturing or stocking the following products: concentrated nitric acid, concentrated acetic acid, higher fatty acids, ammonia and ammonium salts, formaldehyde, hydrogen peroxide, and very many organic products.

In the food industries the most important uses for aluminum are in the dairy industry and related industries, as well as in sugar production, in brewing operations, and in the manufacture of oils. These uses of aluminum extend from small sieves to even the largest storage tanks.

In the agricultural industries spray nozzles for applying pest control products may be mentioned, as well as lightweight movable pipes for irrigation, small equipment on farms, silos for grain and fodder, and machines for drying fodder. Aluminum is also widely used for covering farm buildings (roofing and siding).

CONTAINERS

Aluminum may be used to hold gases under pressure (in gas cylinders), liquids (eg. capsules for bottles, milk jars, beer kegs), pastes (collapsible tubes made by impact extrusion to contain such products as dental paste or mustard), foodstuffs (aluminum

foil, cans), and pharmaceutical products (rigid sheaths). Aluminum foil, which has a thickness of 0.005 to 0.011 mm, has completely replaced silver paper, or tinfoil.

ELECTRICAL INDUSTRIES

When commercial aluminum (99.7% pure) has been annealed, its electrical conductivity equals approximately 63.5% that of copper (International Annealed Copper Standard, IACS). This value is affected by certain impurities. Table 19 shows the reduction in electrical conductivity, in percentage points, brought about by the presence of 10 parts per million of various impurities in 99.99%-pure aluminum as well as in commercial aluminum (47) (ie, the presence of 10 ppm Mn in 99.99% aluminum reduces the conductivity from 63.5 to 63.43% IACS).

Table 19. Absolute Reduction in Conductivity, %IACS

Impurity (10 ppm)	In 99.99%-pure aluminum	In 99.7%-pure aluminum
Mn	0.070	0.038
Ti	0.070	0.040
V	0.075	0.060
Cr	0.080	0.080

Titanium and vanadium are the most frequently encountered among these impurities. It is therefore common practice to precipitate these elements by treating the liquid metal with potassium fluoborate; this lowers the resistance of the metal by approximately 0.038 microhm-cm. Because of this low resistance aluminum has been used as an electrical conductor not only for overhead electrical lines but also in the form of bars and insulated cables, as well as in wires and ribbons for coil windings.

For overhead lines, a combination of high electrical conductivity and high mechanical strength is desired. Partial cold working is used to achieve an increase in the ultimate strength to between 19 and 20 kg mm² (27,000 to 28,500 psi) along with low electrical resistance (which must in no case exceed 2.8264 microhm-cm), in addition to frequently providing the cables with a high-strength steel core.

Another solution is to use cables made of wires of aluminum alloy containing 0.6% of Mg and 0.6% of Si. The use of lightweight cables is becoming general in all distribution systems where the tension does not exceed 90,000 volts, making it possible either to reduce the number of transmission towers with the same sag or to erect lower towers with less sag of the conductor cable.

In central stations and substations bus bars are increasingly being made of aluminum in the form either of flats or of other sections which have a high moment of inertia. For insulated cables, aluminum is used not only as a conductor but also instead of lead as a protective sheath. Aluminum wire strands insulated by a layer of anodic coating have a breakdown voltage between the wire strands of up to 250 volts. This insulation is maintained even at temperatures of 500°C. In this way compact windings can be formed in which heat is easily dissipated. Such windings have been used for load-lifting electromagnets and for the coils of magnetic brakes. Windings are also made with thin insulated aluminum foil, especially for brakes.

Another use for aluminum foil is in making electric condensers. The aluminum foil is first etched in the presence of chloride ion, in order to greatly increase its effective

surface area, and is then coated with a layer of oxide by anodic oxidation in a borate bath.

A very simple way of constructing the rotors of squirrel-cage motors is to cast aluminum into the slots of the magnetic circuit.

Finally aluminum is used in electronics. Thus, it serves to make such articles as nickel-coated printed circuits (by the Kanigen process), television antennas, and wave reflectors.

MECHANICAL CONSTRUCTION

The superior mechanical characteristics of certain heat-treated aluminum alloys have led to their use in constructional work where lightness needs to be combined with mechanical strength.

Table 20. Aluminum Alloys for Constructional Work (at Low Temperatures)

U. S. alloy and temper	Temperature		Yield strength ^a	Ultimate strength ^a	Elongation, %
	°F	°C			
2024-T3	25	78	47.7	68.0	18
	-196	-320	64.9	87.0	22
	-253	-423	73.1	110.0	17
2219-T62	25	78	39.0	58.3	11
	-196	-320	50.3	74.1	14
	-253	-423	54.0	92.2	14
6061-T6	25	78	40.8	44.9	14
	-196	-320	48.6	61.0	23
	-253	-423	55.3	75.8	18
5052-H38	25	78	40.0	45.1	7
	-196	-320	48.0	62.6	25
	-253	-423	54.7	89.7	32
7075-T6	25	78	45.0	46.5	1
	-196	-320	51.6	52.3	1
	-253	-423	61.0	65.6	1

^a In 1000 psi.

Table 21. Aluminum Alloys for Constructional Work (at High Temperatures)

U. S. alloy and temper	Temperature		Yield strength ^a	Ultimate strength ^a
	°F	°C		
2219-T6	20	68	44	61
	150	300	40	52
	200	390	33	41
	250	480	24	30
	300	570	16	21
	350	665	7	12
2618-T6	20	68	47	63
	150	300	45	56
	200	390	38	50.5
	250	480	27	37
	300	570	17	24
	350	665	6	11

^a In 1000 psi.

The alloys shown in Table 20 offer the advantage of retaining very good mechanical strength at low temperatures. At high temperatures, it is general practice to use alloys which either have a higher copper content, as does 2219, or to which (1%) nickel has been added, such as 2618 (see Table 21). Above 250°C, however, the mechanical characteristics suffer a heavy drop and this limits their use.

At high temperatures, the best mechanical properties may be obtained by dispersion of the oxide in the aluminum itself or in its alloys. This is done by sintering aluminum powder which has previously been oxidized so as to include from 8 to 15% of oxide (48). This powder, when cold-pressed, sintered at 500°C, and finally extruded, yields a metal called SAP (the Swiss designation for Sintered Aluminum Powder, known in the U.S. as APM, or Aluminum–Powder Metallurgy). The characteristics of this metal are shown in Table 22.

Table 22. Characteristics of Sintered Aluminum Powder

Temperature		At stated temperature ^a			At room temperature ^b		
		Yield strength ^c	Ultimate strength ^c	Elongation, %	Yield strength ^c	Ultimate strength ^c	Elongation, %
°F	°C						
68	20	43	54	7	41.5	4.3	7
212	100	40	45.5	8	40	41.5	6
390	200	34	37	7	38.5	41	6
570	300	27	30	4	38	41	6
750	400	20	21	1	37	40	6
930	500	13	13	0	36	37	5

^a See stub column (same table).

^b After heating.

^c In 1000 psi.

This metal (SAP) is difficult to weld and can only be joined by flash welding. It is used for making cylinders for jet deflectors in missiles and as a canning and structural material in nuclear reactors.

The low modulus of elasticity of aluminum (7000 kg/mm², or 10,000,000 psi) means that structures made from it are more susceptible to buckling than, for instance, steel. This deficiency must be compensated for by giving the pieces a high moment of inertia.

Aluminum alloys are used for beams, structures, bridges, and hoisting equipment; a very important structural application is in the field of transportation, where they are used to make cars, truck bodies, railroad cars, and many parts of automobile engines.

These alloys are the most important of all materials used in aircraft construction as long as the heating due to high speeds is not excessive. Whereas prior to and during World War II the alloys 2024 and 7075 were those mainly in use, the trend in the construction of supersonic aircraft is in the direction of alloys of the type 2219 and 2618, whose mechanical properties are little affected by temperatures of 130 to 150°C, even over periods of several tens of thousands of hours.

In shipbuilding increasing use is being made of aluminum alloys, especially Al–Mg alloys, which have become recognized as excellent materials for marine purposes. Their use makes it possible to improve the stability and performance of ships by lightening their superstructures. The liners “United States” and “France” each embody several hundreds of tons of aluminum, not counting the metal used in the

furniture and decorations. Aluminum vessels for the transport of alumina are in service both in Europe and in the United States. Lifeboats, miscellaneous accessories, and fish tanks are built of aluminum alloys.

Lighter railroad equipment obtained by the use of such alloys makes it possible to increase the loading capacity of freight cars and the comfort of passenger coaches without affecting the cost of traction. At the same time the reduced weight of the rolling stock brings economies in their maintenance and in that of the road. Aluminum is also employed for the construction of bulk freight cars, such as covered hoppers and gondolas, with the effect that the payload becomes equal to more than four times the tare.

In automobile construction aluminum is beginning to be used for all or parts of passenger cars, including decorative trim, transmissions, and engines. Alloy 5052 and an alloy of the 2117 type are often employed for this purpose. In industrial vehicles, such as trucks and trailer trucks, the use of aluminum makes it possible to increase the transport capacity by 10 to 20%.

Aluminum plays a part in the construction of engines, not only by reason of its thermal properties but also because of the ease with which its alloys may be machined. For all components which have to withstand high temperatures or where the coefficient of expansion has to be as low as possible, frequent use is made of Al-Si alloys. The coefficient of thermal expansion, between 20 and 100°C, is 24×10^{-6} per °C for pure aluminum and 17.5×10^{-6} for the alloy containing 22% Si. The variation is practically linear.

Aluminum alloys can also be used for bearings. The ones most widely employed for this purpose are those containing tin (6%) and copper (2%).

In the compressors for jet engines, the blades in the first stages of the compressor are made of alloy 2618.

BUILDING

Aluminum has long been in use as a roofing material, in the form of strips, corrugated sheets, or prefabricated units. These last may, in certain cases, be made self-supporting. Extrusions and, to a lesser extent, sheet have also been widely used in curtain wall construction in office and commercial buildings. Curtain walling may be either painted or covered with an anodic coating. It is associated with foamed plastics to make lightweight panels that provide good thermal insulation. Deeply corrugated strips make possible the economical and speedy construction of partitions for workshops and studios. The material is very well suited to the construction of factory buildings. Light frameworks built up from aluminum sections permit larger spans and sometimes make it possible to increase the height of buildings. Light alloys have, of course, many applications in the interior fitting of domestic buildings, where they lend themselves to very varied decorative effects. They are also very suitable for making metal furniture.

POWDER AND PAINT

Aluminum powder is obtained by grinding up waste aluminum foil or by atomizing the liquid metal in a stream of gas. The grinding may be done in a ball mill or in a stamp mill in a slightly oxidizing atmosphere (4 to 6% O₂) so as to permit the metal to protect itself and to avoid spontaneous ignition of the metal in air; at the same time, the oxidation must not be strong enough to cause combustion or

explosion inside the mill. An addition of 2% stearic acid facilitates the grinding and makes it safer. Crushing in a liquid, usually mineral spirits, gives a paste that is easy to use.

Powder or paste mixed with a suitable vehicle makes paints which have a high covering power and which offer excellent protection against corrosion: The flakes of aluminum form an overlapping structure, similar to the tiles of a roof. Their high reflecting power is turned to advantage for covering tanks that contain volatile products, as the resulting decrease in the temperature of these tanks reduces the loss of liquid. For these two reasons, aluminum powder or paste is also very suitable for the protection of timber. (See also Coatings, industrial; Pigments; Paints.)

Test Methods

There is no mechanical or physical test peculiar to aluminum alloys.

ANALYTICAL METHODS

The chemical proportions of impurities or additives are determined by various methods of chemical analysis, of which only some general indications can be given here.

Gravimetric Analysis. The most useful application for this is in determining the proportions of the following elements:

- magnesium, weighed as ammonium magnesium pyrophosphate
- silicon, weighed as silica
- zinc, weighed as the thiocyanate of zinc and mercury, $\text{ZnHg}(\text{SCN})_4$
- nickel, weighed as the dimethylglyoxime derivative

Generally, it is planned to avoid having to determine simultaneously the proportions of different elements in the same sample.

Electrogravimetric analysis is used for copper, lead, and nickel, provided they are present in sufficient quantity (usually more than 0.10%).

Volumetric Analysis. This is used to determine the proportions of the following:

- chromium, by reduction with Mohr's salt, $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$
- manganese, by reduction with arsenic acid
- iron, by reduction with titanium trichloride
- zinc, by titration with Complexon III (or Trilon), the disodium salt of EDTA

This type of analysis is rapid but not very sensitive.

Colorimetry. This method makes it possible to determine very small contents (0.01%) of the following, in small samples (0.5 g):

- iron, as thiocyanate (red)
- manganese, as permanganate (violet)
- copper, as the ammoniacal complex (blue) or the complex with diethyldithiocarbamate (brown)
- titanium, as peroxide (yellow)
- vanadium, as peroxide (yellowish-brown)
- silicon, as phosphomolybdate (yellow)

Fluorimetry is scarcely used; its only application is to detect traces of beryllium by the Morin technique. In general, colorimetric analysis is sufficiently quick and specific to afford control over nearly all the constituents and impurities that occur in light alloys. In many laboratories it is used to the exclusion of any other chemical method.

Spectrography. This method has come widely into use by reason of its speed, specificity, and accuracy. It is universally adopted for control of the metal in the melting furnaces before casting.

Generally speaking, it depends on the spark spectrum and on the examination of spectra in the ultraviolet region. The spectrum is detected and measured either by means of a sensitive photochemical emulsion or by direct photometry by means of photoelectric cells.

The intensity of the radiation is compared with that of standard samples that have been analyzed carefully by classical methods of analysis. This method of control is the most frequently used at present.

METALLOGRAPHY

Metallographic Examination. The most common reagent used to attack aluminum and light alloys is a 0.1 to 10% aqueous or alcoholic solution of hydrofluoric acid (Bislee and Czochralski's reagent). Better results, however, are obtained by adding either hydrochloric acid (Flick's reagent (49), made up of 10% HF, 15% HCl, and 75% H₂O) or, in the case of alloys containing copper, hydrochloric acid with nitric acid (Dix and Keller's reagent (50), containing 1% HF, 2.5% HNO₃, 1.5% HCl, and 95% H₂O). In some cases, especially where it is desired to show up the grain boundaries in Al-Mg alloys, an aqueous solution of 5% orthophosphoric acid is preferred.

Where it is a question of detecting peculiarities of the solid solution itself, a reagent may be used which attacks the corroded micropatterns (such as Wyon's reagent (51), as in the sample: 37% HNO₃, 3% HF, 20% HCl, 35% ethyl alcohol, and 5% Teepol surfactant). This makes the shapes of the subgrains visible. The orientation of the grains is brought out by coarser corrosion patterns at the geometric outlines (the reagent used is Lacombe and Beaujard's (52), ie, 47% HNO₃, 50% HCl, and 3% HF).

Heterogeneities in composition, especially with solid solutions of Al-Mg, are revealed either by light anodic attack in a phosphochromic medium (Segol's method (53)) or by the use of Changarnier and Calvet's reagent (54), which consists of 4% KMnO₄ and 2% NaOH in water.

Electrolytic polishing of micrographic samples is easily carried out by means of an automatic apparatus such as the Disa-Electropol. Bath A2 contains 2 parts of perchloric acid ($d = 1.20$), 7 parts of ethyl alcohol, and 1 part of butyl Cellosolve; the operation is carried out at 45 volts for two seconds.

The electron microscope may be used to examine the layer of oxide which is produced by anodic means (ammonium oxalate) and which is removed in a solution of mercuric chloride. Examination by transmission is facilitated by the use of metallic preparations thinned electrolytically by means of the Disa-Electropol (the method of Mirand-Saulnier (55)).

Macrographic Examination. A mixture of aqua regia and hydrofluoric acid is generally used to reveal the grain of the metal. There also are specific reagents for

each family of alloys. For instance, alloys containing copper are treated with an aqueous solution containing 10% H_2SO_4 and 5% HF , after which the attacked surface is treated with a 50% solution of nitric acid. For alloys containing zinc a choice is possible between an aqueous solution of 10% H_3PO_4 and 5% HF or a 20% aqueous caustic soda solution.

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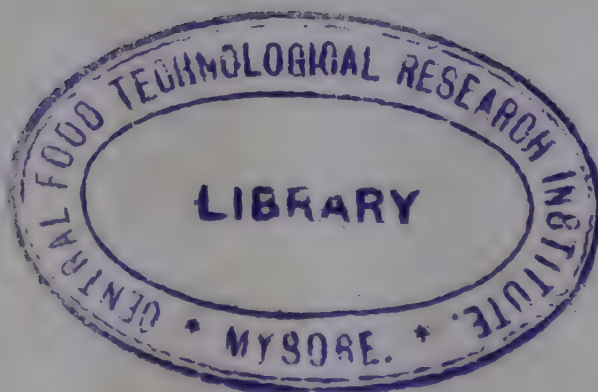
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